GIC-EFCATS 2025 PhD Winter School

CATALYZING SUSTAINABILITY:
Navigating the 2030 Agenda

27th - 31st January 2025

L'Aquila, Italy

Book of Abstracts

Introduction

Catalysis in modern society is a driving force, accounting for a significant part of the global gross domestic product (GDP). Catalytic processes also occur since the beginning of life on Earth, inside each living being, from the single cell up to the largest living organisms. However, since the late 19th Century, the concept of catalysis has been fundamentally associated to industrial processes development.

With the new millennium, the emerging environmental issues, together with changes in geo-political contexts, forced mankind to face new scientific challenges, thus pushing the direction of human development towards greener and more sustainable solutions. Society then rediscovered catalysis beyond the industrial applications, inspired from nature by using light, enzymes, or small effective molecules.

Greener and more sustainable catalytic processes began to complement the traditional ones, spreading innovation and excellence through all the branches of the catalysis realm. The idea standing behind the school is then to promote and enhance these connections between traditional and photo-, organo-, bio-catalysis: their synergy is essential to address the global challenges posed by the Sustainable Development Goals (SDGs) of the UN2030 agenda.

Our goal is to engage all participants, through direct interactions between speakers and students, in a series of state-of-the-art topics in the field of catalysis, promoting an interdisciplinary and innovative approach to addressing the global challenges of our time.

Timetable and Invited Speakers

	27/01/2025	28/01/2025	29/01/2025	30/01/2025	31/01/2025
09:00-10:30		Photoexcitation of catalytic intermediates: a powerful tool for asymmetric catalysis - *Paolo Melchiorre* *(University of Bologna)*	Embedded catalysts: a route to chemical sustainability - *Paolo Fornasiero* *(University of Trieste)*	Mechanocatalysis - Catalysis in Ball Mills - *Lars Borchardt* *(Ruhr-Universität Bochum)*	Catalysis & Industry, combination of mutual boosts: a case study - *Mattia Melloni* *(Versalis)*
10:30-11:00		Coffee break	Coffee break	Coffee break	Coffee break
11:00-12-30		Photoredox Catalysis - Radical Reactivity Sees the Light - *Giacomo Crisenza* *(University of Manchester)*	Single atom and metal-free catalysts: a framework for metal atom economy in catalysis - *Michele Melchionna* *(University of Trieste)*	About Mechanochemistry - How to transfer catalytic reactions to the ball mill - *Wilm Pickhardt* *(Ruhr-Universität Bochum)*	Sustainability in 2nd Gen Process Development, A Case study - *Robert Davidson* *(Pfizer)*
12:30-14:00		Lunch + Poster session	Lunch + Poster session	Lunch + Poster session	Closing remarks + Prizes
14:00-15:00	Registration	Free Time	Free Time	Free Time/L'Aquila guided tour	
15:00-16:30		Exploring catalytic reaction networks with machine learning - *Christoph Scheurer* *(Fritz-Haber Institute)*	Opening the Editor's Black Box - Writing Tips and More - *Haymo Ross* *(Editor-in-Chief of Chem. Eur. J.)*		
16:30-18:00		The twists and turns of biocatalysis - *Francesca Paradisi* *(University of Bern)*	Magnetocatalysis: principles and scope - *Bruno Chaudret* *(University of Toulouse)*		
18:00-18:30	Opening Ceremony	Coffee break	Coffee break		
18:30-20:00	Catalysis as the Key Science and Technology for Green Chemistry of the Future - *Walter Leitner* *(Max Planck Institute)*	Insight and application of enzyme immobilization technology and flow biocatalysis - *Martina Contente* *(University of Milano)*	Magnetocatalysis - two case studies: methanation and ammonia synthesis - *Pierre Fau* *(INSA Toulouse)*		
20:00-21:30	Welcome party	Dinner	Dinner	Social Dinner	

INDEX

Poster Contributions..7

P1: BIOCHAR AS A CATALYST SUPPORT AND ACTIVATION METHODS

Davide Baldassin,[1] **Lilia Longo,**[1] **Alessandro Di Michele,**[2] **Michela Signoretto**[1]

[1] CATMAT Lab, Ca' Foscari University Venice, 30174 Venice, Italy
[2] Department of Physics and Geology University of Perugia, Via Pascoli, 06123 Perugia, Italy
davide.baldassin@unive.it

Pyrolysis can be an effective way to process agricultural and other organic waste into useful products. Pyrolysis is the thermolytic transformation of the biomass, which results in different products: biogas, bio-oil and biochar (the gas, liquid and solid fractions, respectively) [1]. The solid phase is a promising carbon-rich material which could be applied as soil amendment, as adsorbent for contaminant reduction in soil and water, as gas adsorbent, in supercapacitors and in catalysis. Biochar can be used as a metal nanoparticle-based catalyst support, making use of its surface functional groups which can improve anchorage of the active metal phase, such as carboxyl, hydroxyl, amino and lactone groups [2]. However, biochar doesn't always exhibit a high surface area and well-developed porosity necessary for the efficient dispersion of the nanoparticles, needing to be activated first [3].

In this study, we examined how various activating agents affect biochar derived from rice husk, a common agricultural byproduct, processed via slow pyrolysis. To obtain high surface area carbons suitable as supports for metal nanoparticles, the effects of both physical agents (steam - ARS, CO_2 - ARC) and chemical agents (KOH - ARK, H_3PO_4 - ARP) were compared. They were employed as support for Pd nanoparticles using a deposition-precipitation method and tested in benzaldehyde hydrogenation, evaluating reactant conversion and hydrogenation product yield (benzyl alcohol BAL and toluene TOL). Results indicated that the catalyst supported on the KOH-activated biochar was the best performing with the highest TOF and higher yield of toluene. To understand the differences in performance, the catalysts were characterized using various techniques, including N2 physisorption, CHNS elemental analysis, SEM, TEM, and MP-AES.

---

[1] J. Wang, S. Wang, *Journal of Cleaner Production* **2019**, *227*, 1002-1022.

[2] L. Longo, S. Taghavi, M. Riello, E. Ghedini, F. Menegazzo, A. Di Michele, G. Cruciani, M. Signoretto, *Catalysis Today* **2023**, *420*.

[3] J. Lee, K. Kim, E. Kwon, *Renewable and Sustainable Energy Reviews* **2017**, *70-79*.

P2: TRANSFER HYDROGENATION OF FURFURAL UNDER CONTINUOUS FLOW CONDITIONS BY SHVO CATALYST

Maitê Barros Campos,[1] **Luís Adriano Santos do Nascimento**[1], **Emilia Paone**[2], **Giulia Brufani**[2,3], **Chiara Lenzi**[4], **Andrea Piazzi**[4], **Rita Mazzoni**[4], **Luigi Vaccaro**[3], **Francesco Mauriello**[2]

[1] *Postgraduate Program of Biotechnology, Federal University of Pará, Brazil*
[2] *Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, Italy*
[3] *Dipartimento di Chimica Biologia e Biotecnologie, Università degli Studi di Perugia, Italy*
[4] *Dipartimento di Chimica Industriale, Università degli Studi Alma Mater Studiorum di Bologna, Italy*
maite.campos@icb.ufpa.br

Furfural is a cornerstone biomass-derived platform chemical with numerous industrial applications[1-2]. Traditional hydrogenation techniques, employing molecular hydrogen in batch reactors, face several limitations, including high pressure requirements and harsh reaction conditions. Addressing these challenges, our research utilizes the Shvo catalyst [3], a renowned ruthenium-based complex, in a continuous-flow system for the catalytic transfer hydrogenation (CTH) of furfural [4]. This study marks the first use of the Shvo catalyst in continuous-flow reduction of furfural, promoting a safer, more efficient, and sustainable approach for CTH process of biomass derived molecules. The use of 2-methyloxolane (MeOx) as a co-solvent improved the solubility of the Shvo catalyst, enabling its application in this reaction. The results showed that under optimized conditions (150°C, flow rate of 250 µL/min, and 1.5 equivalents of 2-propanol), the process achieved a high conversion rate of 97.4%, converting furfural to furfuryl alcohol. Other hydrogen donors were tested and showed lower efficiency than 2-propanol, highlighting the need for an optimal hydrogen donor. Varying the equivalents of 2-propanol (1, 1.2, 1.5) and the temperatures (90 ºC, 120 ºC, 150 ºC) demonstrated a clear trend: higher equivalents and temperatures generally improved the conversion efficiency. These results illustrate the importance of hydrogen donor availability and temperature in optimizing the catalytic process, highlighting a crucial factor in the design of continuous-flow chemical reactions. After reaction, the Shvo catalyst can be easily recovered by precipitation in hexane and retains high activity even after five cycles. Different substrates were also tested, confirming the applicability of this process to a broad range of substrates. In conclusion, this research confirms the Shvo catalyst's viability for continuous-flow applications and highlights its potential for sustainable industrial-scale chemical synthesis, representing a significant advance in green chemistry.

Acknowledgements: *This work has been funded by the European Union–NextGenerationEU under the Italian Ministry of University and Research (MUR) within PNNR MUR-M4C2-Investimento 1.5 - "Ecosistemi dell'Innovazione". In particular, authors thanks projects "Ecosistema TECH4YOU", "Ecostistema ECOSISTER" and "Ecosistema VINITALY".*

---

[1] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev*. **2014**, *114*, 1827–1870.
[2] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev*. **2020**, *49*, 4273–4306.
[3] B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev*. **2010**, *110*, 2294–2312.
[4] M. J. Gilkey, B. Xu, *ACS Catal*. **2016**, *6*, 1420–1436.

P3: Hydroconversion of advanced non-conventional feedstocks (ADFNCs): impact of co-processing

<u>Arij Ben Hassine</u>,[1] M. Joana N. Correia,[2] Pedro S.F. Mendes[1]

[1] *CQE, Centro de Química Estrutural , Instituto Superior Técnico, Universidade de Lisboa, Portugal*
[2] *CERENA, Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Portugal*
arij.ben.hassine@tecnico.ulisboa.pt

With the world transition to cleaner energy strategies, renewable fuels are crucial to meet sustainability goals, especially in hard-to-decarbonize sectors like aviation. However, ensuring a steady supply of suitable resources is a growing concern. Co-processing diverse, non-conventional feedstocks such as used cooking oils, biomass and waste-derived pyrolysis oils, offers a promising solution by enhancing flexibility and resource availability[1]. The varying properties of these feedstocks, however, might complicate their integration into fuel production processes, requiring careful optimization to achieve needed quality for a drop-in ASTM-compliant Sustainable Aviation Fuel (SAF). This work is focused on studying the impact of co-processing advanced feedstocks aiming to understand how co-processing might deviate from simple mixture expectations. To understand this impact, a kinetic and a reactor model was built to simulate possible factors involved in mixture effects. A simplified approach is first considered with pure compounds to represent each feedstock (UCO-model compound and lignin-model compound) ultimately aiming to simulate more realistic compositions. The figure below illustrates potential impacts of co-processing. Preliminary findings indicate that co-processing often deviates from a simple additive behavior, resulting in a final product composition governed by the more reactive component. This suggests a complex interplay between the feedstocks during co-processing[2], leading to behaviors that differ from processing them individually. Understanding these effects is essential for optimizing co-processing conditions and achieving the desired product quality meeting jet fuel standards.

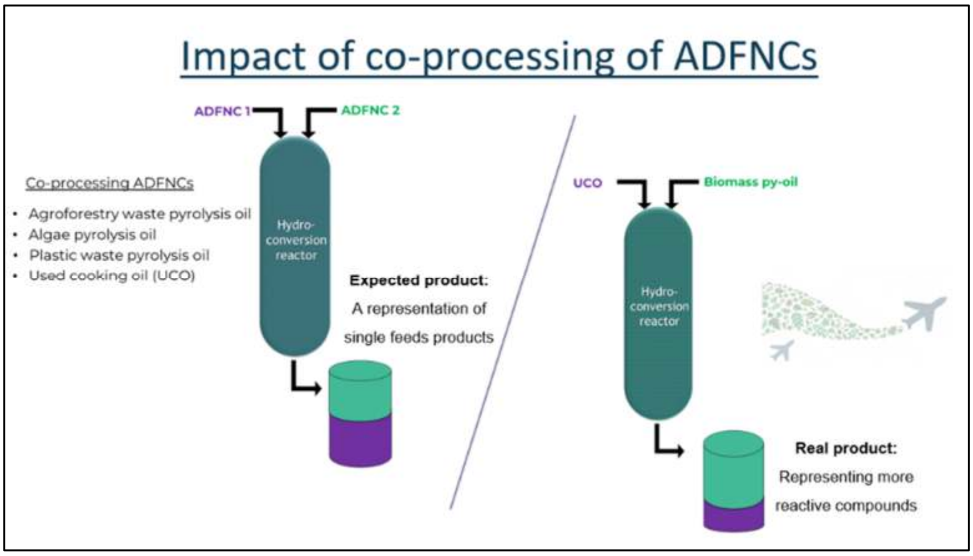


Figure 1*: Impact of co-processing advanced feedstocks*

[1]Paiva Pinheiro Pires, A., Olarte, M., Terrell, E., Garcia-Perez, M. & Han, Y. *Energy and Fuels* **37**, 2100–2114 (2023).
[2]Han, Y., Pires, A. P. P. & Garcia-Perez, M. *Energy and Fuels* vol. 34 (2020).

P4: CO_2 hydrogenation to Methanol over Cu-In_2O_3-Al_2O_3 based catalysts

Andrea Bertuzzi,[1] **Giuseppe Fornasari**,[1] **Patricia Benito**[1], **Alberto Renato de Angelis**[2], **Giacomo Filippini**[2]

[1] *Dipartimento di Chimica Industriale "Toso Montanari", viale del Risorgimento, 4, Bologna 40136, Italy*
[2] *Centro di Ricerca Eni, via Felice Maritano, 26, San Donato Milanese 20097, Italy*

andrea.bertuzzi6@unibo.it

At the industrial level, the most employed catalysts for MeOH synthesis are based on the Cu/ZnO/Al_2O_3 (CZA) system. Despite its high activity, CZA ternary catalysts are still limited by low MeOH selectivity, and mostly by the rapid deactivation related to Cu and ZnO sintering.[1]

Many studies are focusing their attention on alternative metal oxides (e.g. In_2O_3, Ga_2O_3 etc.), as they demonstrated an improved stabilization and an enhanced MeOH selectivity.[2,3]

In this work, we studied the activity of Cu-In_2O_3-Al_2O_3 based materials in CO_2 hydrogenation to MeOH. A one-step co-precipitation synthesis method was employed. In particular, two series of catalysts with different Cu content were prepared, maintaining fixed the Indium loading. Among each batch, two basic oxide promoters were added to evaluate their effect upon catalytic performances.

CO_2 hydrogenation to MeOH was conducted at industrial relevant pressures in a continuous gas phase plant on the previously in-situ activated materials. The results showed improved MeOH productivities in presence of the oxides. An ex-situ characterization study allowed us to preliminary explain the activity trends, according to the structural and chemical modifications provoked by the two different dopants.

---

[1] Beck, A., Newton, M. A., Water, L. G. A. van de & Bokhoven, J. A. van. The Enigma of Methanol Synthesis by Cu/ZnO/Al2O3-Based Catalysts. *Chem Rev* (2024).
[2] Ye, J., Liu, C., Mei, D. & Ge, Q. Active oxygen vacancy site for methanol synthesis from CO2 hydrogenation on In2O3(110): A DFT study. *ACS Catal* 3, 1296–1306 (2013).
[3] Wang, J. *et al.* CO2Hydrogenation to Methanol over In2O3-Based Catalysts: From Mechanism to Catalyst Development. *ACS Catal* 11, 1406–1423 (2021).

P5: From models to real waste biomass: a novel and sustainable strategy for ethyl levulinate production

Lorenzo Bonaldi,[1] Claudia Antonetti,[1] Domenico Licursi,[1] Nicola Di Fidio,[1] Anna Maria Raspolli Galletti,[1] Sara Fulignati[1]

[1] *Department of Chemistry and Industrial Chemistry, University of Pisa, Italy*

lorenzo.bonaldi@phd.unipi.it

Levulinic acid (LA) is one of the top 12 most promising bio-derived compounds for generating value-added products. However, due to the essential upgrading processes required for its production, purification and transformation, the cost of LA remains high in the global market. Consequently, research efforts are increasingly focused on developing simpler processes for producing LA derivatives. Ethyl levulinate (EL) meets these criteria, as it can be produced directly from biomass via an acid-catalysed alcoholysis reaction and offers easier purification[1]. Therefore, the present work aimed to produce EL from real waste biomass, by adopting ethanol as a green reagent/reaction medium and sulfuric acid as cheap homogeneous catalyst. Initially, the study focused on using sucrose as a model substrate, optimizing EL formation through a multivariate approach to assess the synergistic effects of temperature, reaction time, and sulfuric acid loading. In this way, the highest EL yield of 54.6 mol% was achieved with an H2SO4 loading of 0.5 wt% at 158 °C for 4.6 h, minimising the formation of side products such as diethyl ether (DEE). Subsequently, the optimal conditions identified were applied to the valorization of thick juice (TJ)[2], an intermediate sugar refinery product with high sucrose content, resulting in a favourable EL yield (37.6 mol%). Based on these results, the work subsequently shifted to the valorisation of real waste biomass, specifically bread waste (BW). As one of the largest contributors to global food waste[3], BW appears as an attractive low-cost raw material for EL production due to its high starch content. Thus, the ethanolysis of BW was investigated using a One-Factor-at-a-Time (OFAT) approach, adopting H2SO4 as the catalyst, resulting in good EL yields of about 40 mol%. In conclusion, this study utilized sucrose as a model substrate in ethanolysis reactions for EL production and the obtained results enabled to study the transition to the valorization of real substrates, such as an industrial by-product (TJ) and a food waste (BW) contributing to a more sustainable approach to EL production.

Acknowledgements: *The authors are grateful to the European Union and Italian Ministero dell'Università e della Ricerca for the financial support provided through the PNRR project NEST. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), (CUP I53C22001450006) Spoke n. 3 BIOENERGY & NEW BIOFUELS FOR SUSTAINABLE FUTURE*

---

[1] *A. M. Raspolli Galletti, C. Antonetti, S. Fulignati, D. Licursi, Catalysts,* ***2020,*** *10, 1221.*

[2] *R. M. Abdilla-Santes, W. Guo, P. C. A. Bruijnincx, J. Yue, P. J. Deuss, H. J. Heeres, ChemSusChem,* ***2019****, 12, 4304.*

[3] *V. Kumar, P. Brancoli, V. Narisetty, S. Wallace, D. Charalampopoulos, B. Kumar Dubey, G. Kumar, A. Bhatnagar, S. Kant Bhatia, M. J. Taherzadeh, Bioresour. Technol.,* ***2023****, 369, 128449.*

P6: CO_2 Degradation via Photocatalysis Using Biomass-Derived Carbon Dots and TiO_2

Teresa Botrè,[1] **Giorgia Ferraro**,[1] **Federica Menegazzo**,[1] **Michela Signoretto**,[1]

[1] Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RU of Venice Via Torino 155, 30172 Venice, Italy

teresa.botre@unive.it

The growing urgency to address CO_2 emissions has spurred the development of sustainable methods for its degradation, with photocatalysis emerging as a promising approach[1]. This work highlights the utilization of two biomass wastes strictly connected to Italy's industrial excellence: hazelnut shells and leather residues. Italy ranks as the second-largest global producer of hazelnuts, and its leather industry is renowned as a worldwide leader. Both materials were processed via pyrolysis, with the resulting bio-oil employed to synthesize carbon dots (CDs), which are gaining attention as photocatalysts due to their stability, efficient charge transfer, and low toxicity[2]. The CDs were then associated as co-catalysts into TiO_2 to enhance its photocatalytic properties under solar light.

The catalysts were prepared with a hydrothermal treatment using water as solvent and then characterized through HRTEM, XRD, N2 physisorption, and DRS analyses. The photocatalyst were tested for CO2 degradation under solar radiation using a gas phase batch reactor, revealing a substantial enhancement in activity compared to pristine TiO_2, the benchmark photocatalyst[3].

Hazelnut shell-derived carbon dots showed the best photocatalytic activity under solar light, reaching TON of 7,9 µmol/gcat. Then superior performance of the biomass-derived catalysts was attributed to the synergistic effects of the CDs, including improved light absorption, enhanced charge separation, and a reduced band gap energy.

This study underscores the dual environmental and economic benefits of transforming Italy-specific industrial byproducts into high-performance photocatalysts. By valorising abundant local wastes, this approach contributes to effective CO_2 mitigation, tackling a critical global environmental challenge while promoting a circular economy. The research aligns with the EU's 2030 Agenda for sustainability and offers scalable, environmentally friendly solutions to support the energy transition.

Acknowledgements: *This study was funded by the European Union – NextGenerationEU, in the framework of iNEST – Interconnected Nord-Est Innovation Ecosystem (iNEST ECS_00000043 – CUP H43C22000540006)*

---

[1] D.K. Dogutan and D.G. Nocera, *Chem. Res.* **2019**, 52, 3143-3148.
[2] G. Ferraro et al., *Applied Catalysis O.Open*, **2024**, 192, 206942.
[2] H. Zhao et al., *J. Materiomics*, 2017, 3, 17-32.

P7: Ni/Al_2O_3 EMBEDDED CATALYST FOR METHANE DRY REFORMING

Rachele Braido,[1] Giulia Da Pian,[1] Irene Martin,[2] Giuseppe Cruciani,[3] and Michela Signoretto[1]

[1] Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RUVe Via Torino 155, 30172-Venezia, Italia
[2] Functional Nanosystems, Italian Institute of Technology (IIT), Via Morego 30, 16163 Genoa Italy, and Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 34, 10129 Turin Italy
[3] Department of Physics and Earth Science, University of Ferrara, Via Saragat 1, 44122-Ferrara, Italia
rachele.braido@unive.it

In recent decades, research has focused on the goal of finding cleaner energy sources, combined to reducing greenhouse gases emissions as well as capturing ad using these gases. Dry Reforming of Methane (DRM) enters in this field. DRM is a catalytic process that converts two of the most abundant and impactful greenhouse gases - methane and carbon dioxide - into a high-value gas mixture called syngas. Syngas, composed of carbon monoxide and hydrogen, has various applications, including utilization in the Fischer-Tropsch reaction, conversion into fuels, and production of cleaner hydrogen[1], an energy vector that can be used as energy source. Despite recent advances in catalytic systems, DRM is not yet applied at an industrial level, due to two key deactivation issues. The first is the sintering of the metal active phase, which occurs at the high temperatures required by the reaction's endothermic nature. The second is coke deposition on the catalytic surface, related to secondary side reactions[2]. In this work, a particular structure is investigated as a catalytic system for the DRM reaction to solve these deactivation problems. A core-shell-like structure is synthesized to encapsulate nickel within an Al_2O_3 protective layer. This protective layer is designed to shield the Ni active sites from sintering and coke deposition, thereby enhancing the catalyst's stability over time. The obtained catalyst was tested for the DRM reaction at 650 °C in a fixed bed reactor with a GHSV of 12000 h-1, using a CH_4:CO_2:He ratio of 1:1:18, under a total flow of 200 mL/min. Additionally, recycling tests were conducted. The fresh and spent samples were characterized using various techniques such as XRD, SEM, TEM, TPR, TPO, and N_2 physisorption.

---

[1] M. Pizzolato, G. Da Pian, E. Ghedini, A. Di Michele, F. Menegazzo, G. Cruciani, and M. Signoretto, *Reactions,* **2022**, *3,* 634 – 647.

[2] M. Pizzolato, G. Da Pian, E. Ghedini, A. Di Michele, F. Menegazzo, G. Cruciani, and M. Signoretto, *Catalisys Today,* **2023**, *418,* 114041.

P8: New insights into the key role of the thermal treatment of V/P/O catalysts for the selective oxidation of butane to maleic anhydride

Marco Brocchi[1,2], Laura Setti[1], Ludovica Conte[3], Giacomo Luzzati[1], Silvia Luciani[3], Laura Fratalocchi[3], Lorenzo Grazia[3], Carlotta Cortelli[3], Fabrizio Cavani[1,2], Tommaso Tabanelli[1,2]

[1] Department of Industrial Chemistry "Toso Montanari", via Piero Gobetti 85, Bologna, 40129, Italy;
[2] Consorzio INSTM, Research Unit of Bologna, Via Giuseppe Giusti 9, 50121, Firenze, Italy;
[3] POLYNT SPA, Via Enrico Fermi 51, Scanzorosciate, Bergamo, 24020, Italy.
marco.brocchi4@unibo.it

Maleic anhydride (MA) is a versatile molecule due to its three active sites, i.e. two carboxylic groups and a double carbon bond. It is considered an important building block in industrial chemistry, with several applications such as monomers for polyesters and alkyd resins, as well as an intermediate to produce fine chemicals (succinic acid, malic acid, and fumaric acid). Industrially, the production of MA remains solidly linked to the continuous-flow, gas-phase selective oxidation of petrochemical raw materials, Traditionally, benzene was the main substrate used in the production of MA, using vanadium and molybdenum containing catalysts. However, this method presents several drawbacks such as the carcinogenic nature of benzene itself, relatively low atom efficiency (i.e. two C atoms are lost in the form of COx), and high exothermicity. Therefore, benzene is gradually being replaced with *n*-butane (due to lower cost and higher atom economy), while vanadium and molybdenum catalysts have been replaced by vanadium phosphates (V/P/O), which are able to promote the selective oxidation of this linear alkane toward MA exhibiting best results in terms of conversion and yields.

This work explores the thermal treatment of V/P/O catalyst precursors to achieve active and selective catalysts for the oxidation of *n*-butane to maleic anhydride (MA) in a continuous-flow, fixed-bed reactor. Vanadyl pyrophosphate (V^{4+}, VPP), the key catalyst component, is produced together with suitable V^{5+} vanadium orthophosphate ($VOPO_4$) allotropic forms by thermally treating vanadyl hydrogen phosphate hemihydrate (VHP) in various atmospheres and temperature ramps[1]. The characterization conducted using X-ray diffraction, Raman spectroscopy, and reaction testing allowed the identification of optimal conditions for active and selective catalysts. Oxygen is necessary for obtaining VPP and affects the vanadium oxidation state, a crucial parameter for selectivity. Water enhances the crystallinity and conversion of VHP to VPP. An optimized calcination atmosphere (6:10:84 mol% of O_2:H_2O:N_2) ensures 70% MA selectivity at 50% butane conversion at 400 °C [2]. VHP precursors characterized by higher P/V ratios allow to obtain higher MA selectivity when treated at the same calcination conditions.

This study aims to ensure the consistent production of the best-performing catalyst by tuning the calcination conditions based on the precursor's specific pre-calcination characteristics and properties.

---

[1] Setti L., et al. *New insights into the key role of the thermal treatment of V/P/O catalysts for the selective oxidation of n-butane to maleic anhydride.* (2024)

[2] Cortelli C., et al. *Process for the transformation of a vanadium/phosphorus mixed oxide catalyst precursor into the active catalyst for the production of Maleic Anhydride*. (2022). WO2023165735A.

P9: Multi-component reaction promoted by a palladium-gold catalytic-cooperative system

<u>Alessandro Brusa</u>,[1] **Fabio Pesciaioli**,[1] **Armando Carlone**[1]

[1] *Università degli studi dell'Aquila, Italy*
alessandro.brusa@graduate.univaq.it

The multi-component reactions are an important class of chemical reactions; they merge more than two chemical structures together, creating molecular complexity very rapidly, in just one process. Palladium-catalysed and gold-catalysed processes are both recognized as very important for the synthesis of organic structures, and the activation mode typically exploited by these two transition metals are different at a fundamental level.[1] These *orthogonal* catalytic activities can work *cooperatively* in the same system, potentially in multi-component reactions. In particular, the gold-catalysed addition of hydro-nucleophiles (for example alcohols) to alkynes, followed by a palladium catalysed cross-coupling is not reported for *simple* alkynes. Thus, in this project we try to overcome the problems associated the use of halides for cross-coupling, and gold to palladium transmetallation process to create new multi-component reactions (Figure 1).

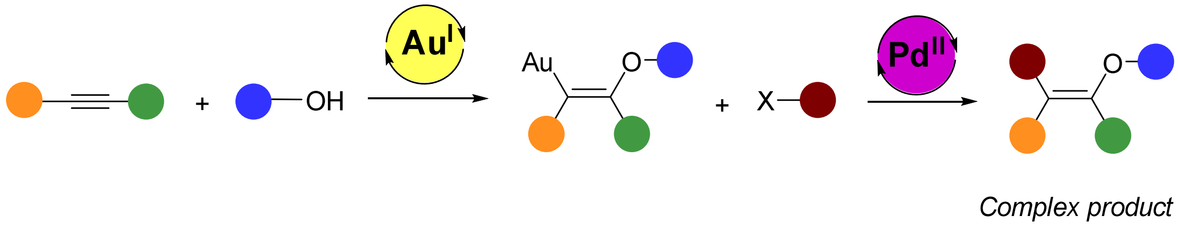


Figure 1: general reaction scheme

The development of these new catalytic processes is carried out as a *separated development*: a single catalytic cycle of one metal (for example gold) is optimized separately, then the catalytic cycle with the other metal is optimized under the same conditions, just changing substrate. The robustness of the process is then tested with cross experiments, to check the compatibility of each reaction component. For example, a possible additive used for the palladium catalysis is used in the gold catalyzed process, to check if there is any interference. Only when everything works separately the two processes are merged together. This helps to understand experimentally the difficult parts of the process, in order to rationally design and fix it.

---

[1] M.Al-Amin, K. E. Roth, S. A. Blum, *ACS Catalysis*, **2013**, *Vol 4*, *Issue 2*, 622-629

P10: Ultrasound-assisted Preparation of Ru- and Pd-Iron Oxide Catalysts for Lignocellulosic Biomass Valorisation

[1] Chiara Bruschetta, [1] Maela Manzoli, [1] Giancarlo Cravotto

[1]Department of Drug Scienze and Technology, University of Turin, Via P. Giuria 9, 10125 Turin, Italy

*chiara.bruschetta@unito.it

Metal oxide nanoparticles achieve the unique properties such as high surface area, excellent mechanical strength, catalytic properties and biocompatibility. For their preparation, wet impregnation, hydrothermal synthesis, thermal decomposition, spray pyrolysis etc. have been traditionally employed. Ultrasound (US)-assisted preparation is known as an alternative pathway to obtain novel materials avoiding high temperature and pressure or prolonged reaction times[1]. The effect of US as an energy source for chemical reactions deals with process intensification,[2] due to an increase in both mass and heat transfer and to the generation of cavitation bubbles undergoing very short and violent collapses within the fluid, giving rise to local hot-spots with high energy.[3] In particular, when used in liquid systems, within the zone of extreme 'mixing' close to the ultrasonic source (i.e. the transducer) the cavitation offers remarkable advantages such as de-agglomeration, particle size reduction, dispersion, homogenisation, emulsification, atomisation, molecular degradation, and an improvement of surfaces.[3] The aim of this work is to evaluate the effect of different US irradiation systems (common ultrasonic bath, ultrasonic probe) during the preparation of ferrite-based[4] Ru and Pd catalysts (*Figure 1*).

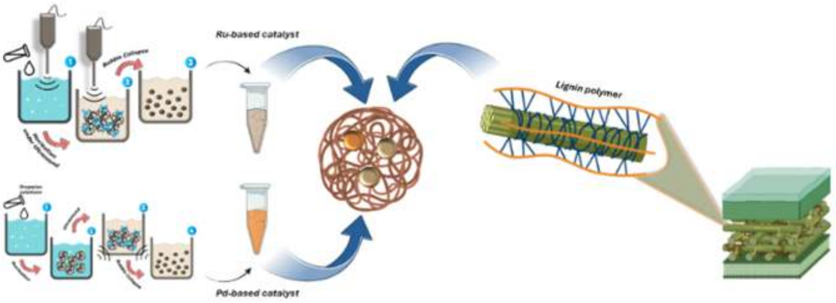


Figure 1. *Synthesis procedure of Ru- and Pd-based catalyst and coupling with lignin polymer extracted from wheat straw*

The structural and morphological changes depending on the adopted US-assisted procedure (in terms of power and duration) have been monitored by XRD and high-resolution STEM coupled with EDS. It was observed that the US-assisted co-precipitation process allowed to obtain a better dispersion of the metals than the application of US after co-precipitation process. These systems were tested in different applications to convert directly lignin or platform chemicals (such as furfural and levulinic acid) derived from cellulose to added-value products. Ongoing preliminary tests are involving these materials, previously chemically bonded with modified lignin, as bio-based catalysts for biomass valorisation within a circular economy approach.

---

[1] H., Xu; B. W., Zeiger; K. S., Suslick; *Chem. Soc. Rev.,* **2013**, 42, 2555
[2] B. G., Pollet, J. T. E., Goh; *Electrochim. Acta,* **2014**, 128, 292–303
[3] B. G., Pollet; *Electrocatalysis*, **2014**, 5, 330–343
[4] A., Hajnorouzia; N., Modaresib; *J. Magn. Magn. Mater.*, **2020**, 505, 166732

P11: Photocatalytic and Photo-Fenton degradation activity of cerium ferrite and g-C_3N_4 nanocomposite

Aneta Bužková,[1] **Radka Pocklanová,**[1] **Martin Petr,**[2] **Josef Kašlík,**[2] **Vlastimil Novák,**[3] **Jiří Pavlovský,**[3] **Robert Prucek,**[1] **Libor Kvítek**[1]

[1] *Department of Physical chemistry, Faculty of Science, Palacký University in Olomouc, Czech Republic*
[2] *Regional Centre of Advanced Technologies and Materials (RCPTM), Czech Advanced Technology and Research Institute (CATRIN), Palacký University in Olomouc, Czech Republic*
[3] *Department of Chemistry and Physico Chemical Processes, Faculty of Materials Science and Technology, Technical University of Ostrava, Czech Republic*
aneta.buzkova@upol.cz

Ferrites are a commonly used material for the Fenton degradation of water pollutants.[1] However, this material can also be used in composites with a photocatalytic substrate such as graphitic carbon nitride (gCN) and thus be used for Foto-Fenton or photocatalytic degradation. The unique properties of these composites, including $ZnFe_2O_4$,[2] $MgFe_2O_4$,[3] $LaFeO_3$[4], and our studied cerium ferrite (CFO) with gCN, are of great interest. This composite not only exhibits Photo-Fenton degradation but also photocatalytic degradation. The CFO can participate in redox reactions thanks to the mixed valence state of cerium (Ce^{3+} and Ce^{4+}). In the photocatalytic degradation of Rhodamine B, a yellow fluorescent intermediate called Rhodamine 110 is created during degradation. Oppositely, during Photo-Fenton degradation, this intermediate does not form. Thus, these two degradation process pathways differ. Interestingly, the effect of RhB solutions' pH also differs in these two types of degradation. The efficiency of photocatalytic degradation decreases with increasing pH. Hence, for pH 4, 96% of RhB is degraded and for pH 10, only 35%. For Photo-Fenton degradation, the influence of pH on efficiency is insignificant, and for all tested pH, the RhB is degraded above 97%.

Acknowledgements: *The authors gratefully acknowledge financial support from Internal Student Grant Agency of the Palacký University in Olomouc, Czech Republic (IGA_ PrF_2024_021).*

---

[1] M. Ismael, *Solar Energy Materials and Solar Cells* **2021**, *219*, 110786.
[2] J. Yan, B. Chai, Y. Liu, G. Fan and G. Song, *Appl Surf Sci* **2023**, *607*, 155088.
[3] S. Qiu, L. Gou, F. Cheng, M. Zhang and M. Guo, *J Environ Manage* **2022**, *321*, 115907.
[4] Y. Ye, H. Yang, X. Wang and W. Feng, *Mater Sci Semicond Process* **2018**, *82*, 14–24.

P12: Exploring LDHs-derived composite performances in photo-thermocatalytic CO_2 methanation

<u>Luca Calantropo</u>[1], M. T. Armeli Iapichino[1], G. Dativo[1], E. La Greca[1,2], S. Sciré[1], R. Fiorenza[1,3]

[1] Department of Chemical Sciences, University of Catania, Italy
[2]Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Italy
[3]Institute for Microelectronics and Microsystems (IMM), National Research Council (CNR), Italy

luca.calantropo@phd.unict.it

The hydrogenation reaction is one of the most widely used routes for CO_2 conversion. However, being an extremely energy-intensive process, new hybrid catalytic processes, such as the photo-thermo catalysis, need to be developed to overcome the disadvantages of conventional thermocatalysis. [1] This is the context of this research work, whose objective is to synthesize new Layer Double Hydroxides-based composite materials by evaluating their photo-thermocatalytic performances in the CO_2 methanation reaction. The LDHs are in fact an excellent candidate for the development of photo-thermocatalytic processes that aim to the conversion of CO_2. This is due to their excellent adsorption properties, their modulable surface basicity, the high surface area that favoured the intercalation of metals within the structure or the deposition in the surface, and the formation of optical band-gaps that allow the activation of the photo-thermocatalytic effects. In this study, ternary LDHs were synthesized by co-precipitation and hydrothermal treatment inserting different metal species such as Ni or Co, as catalytic active species, Mg or Zn, as photocatalytic active species and Al for the structural role. The LDHs were then modified with SiC or Montmorillonite to improve their photo-thermal properties, obtaining new materials able to absorb a larger portion of the solar emission spectrum and to increase the conversion of solar radiation into thermal energy, favouring the methanation reaction through a photo-assisted thermo-catalytic mechanism.[2] Catalytic tests show that SiC significantly increased the photo-thermocatalytic activity of LDH, enhancing yield and selectivity in methane at lower temperatures compared to thermocatalytic tests, while the samples modified with montmorillonite promoted the reverse water gas shift reaction. Future objectives of this work include exploring different compositions for the synthesis of LDH-phyllosilicates composites using Halloysite, Bentonite, Sepiolite and modified Montmorillonite obtained with the addition of CTAB; the synthesis of new LDH-MXene composites to exploit the LSPR effect of MXenes in order to improve the photo-thermocatalytic activity of the materials.

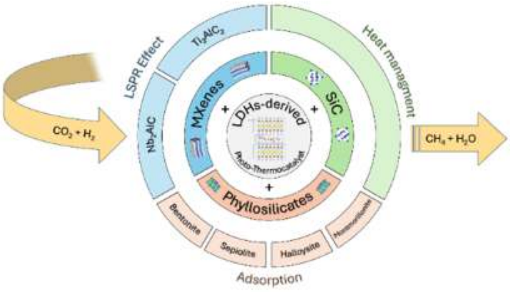


***Figure 1**: Photo-thermocatalytic CO_2 methanation on LDHs-derived composites.*

---

[1] *Y. Guo, T. Li, D. Li, J. Cheng, Renew. Sustain. Energy Rev. 189 **(2024)** 114053*
[2] *S.R. Kulkarni, V.K. Velisoju, F. Tavares, A. Dikhtiarenko, J. Gascon, P. Castaño, Catal. Rev. 65 **(2023)** 174–237.*

P13: Switching from Petro- to Bio-based chemistry: DeOxyDeHydration (DODH) reaction as versatile tool for the production of olefins from natural polyols

M. E. Casacchia,[1] **A. Di Giuseppe**,[1] **M. Crucianelli**,[1] **N. d'Alessandro**,[2] **L. Tonucci**,[2] **A. Mascitti**,[2]
E. Rombi,[3] **M.G. Cutrufello**,[3] **F. J. Platero**,[3] **A. Ruggiu**,[3] **S. Piccinin**,[4] **C. F. Pauletti**[5]

[1]*Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, L'Aquila, Italy*
[2]*Department of Engineering and Geology, University of Chieti-Pescara, Viale Pindaro, 42, Pescara, Italy*
[3]*Dipartimento di Scienze chimiche e geologiche, Università di Cagliari, Monserrato, S.S. 554, Monserrato (CA), Italy*
[4]*CNR-IOM Trieste, Strada Statale 14, km 163,5, Basovizza (TS), Italy*
[5]*Department of Physics, University of Trieste, Via Alfonso Valerio, 2, Trieste, Italy*
mariaedith.casacchia@univaq.it

The transition from petrochemical-based resources to renewable biomass is essential for sustainable chemical production, as the finite nature of fossil fuels continues to drive their depletion. Biomass, rich in oxygen-containing macromolecules, offers a renewable alternative but requires innovative methodologies to integrate its derivatives into industrial processes. Among these, the deoxydehydration (DODH) reaction is a key transformation, converting vicinal diols from bio-based polyols into valuable light olefins, essential intermediates for polymers and fuels. [1,2]

This project focuses on developing safe, green, and cost-effective catalytic systems for the DODH reaction, addressing challenges such as the hydrophilicity of polyols, high oxygen content, and the reaction's dependence on expensive rhenium catalysts.[3] Key objectives include reducing catalyst loading, designing heterogeneous and bimetallic catalytic systems, employing environmentally benign reductants, and exploring alternative solvent systems. Computational studies using density functional theory (DFT) complement these efforts, providing insights into reaction mechanisms and guiding catalyst design.

In this study, the heterogeneous rhenium-based catalysts under investigation for the DODH reaction of selected substrates, are supported on a range of metal oxides, including SiO_2, Nb_2O_5, ZrO_2, and CeO_2, as well as on their binary mixtures such as silica/niobia and ceria/zirconia. The substrates studied to date include diethyl tartrate, 1-phenylethane-1,2-diol, and 1,2-hexanediol.

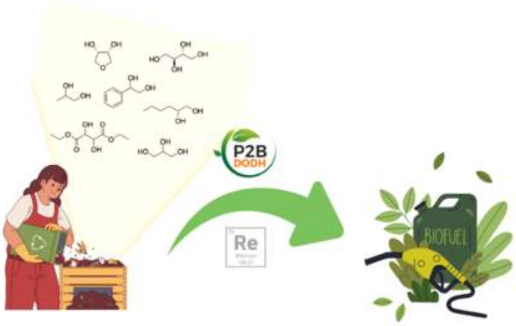


***Figure 1**: Graphical description of the project*

***Acknowledgements**: Financial support from PRIN2022: P2B DODH - CUP: E53D23008340006 is gratefully acknowledged*

---

[1] N.N. Tshibalonza, J.C.M. Monbaliu, Green Chem. 22 (2020) 4801
[2] G. Scioli, L. Tonucci, P. Di Profio, A. Proto, R. Cucciniello, N. d'Alessandro, Sust. Chem. Pharm., 17 (2020) 100273
[3] L.J. Donnelly et al. Chemistry: Asian J. 14 (14) 3782

P14: Harnessing synergy between nanoparticles and single atoms on C_3N_4 ultrananosheets for enhanced hydrogen evolution

Gaia Castellani,[1] **Priti Sharma,**[2] **Štepán ˇKment,**[2,3] **Michele Melcionna,**[1,4] **Radek Zbořil,**[2,3]
Paolo Fornasiero.[1,4]

[1] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy*
[2] *Czech Advanced Technology and Research Institute, Regional Centre of Advanced Technologies and Materials, Palacký University, Olomouc, Czech Republic*
[3]*Nanotechnology Centre, Centre for Energy and Environmental Technologies, VSB−Technical University of Ostrava, Ostrava, Czech Republic*
[4]*Center for Energy, Environment and Transport "Giacomo Ciamician" and ICCOM-CNR Trieste Research Unit, University of Trieste, Trieste, Italy*
gaia.castellani@phd.units.it

Hydrogen (H_2) is considered a promising energy vector and an alternative to the use of fossil fuels.[1] It has been demonstrated that combining single atoms (SA) and nanoparticles (NP) on appropriate supports can create synergistic effects that significantly enhance the performance of metals, leading to improved hydrogen production efficiency.[2]

In this study, we explore the photocatalytic activity of three distinct material configurations based on Pt and Pd. These consist of nanoparticles (M_{NP}), single atoms (M_{SA}), and both single atoms and nanoparticles (M_{SA+NP}), all anchored on ultrananosheets of carbon nitride (UNS) (where M = Pt, Pd).

The synthesis process involved thermal polymerization of dicyandiamide to produce graphitic carbon nitride (*g*-CN), followed by additional thermal treatments to form the ultrananosheets. Metal salts were then adsorbed onto the UNS using $NaBH_4$ as a reducing agent.

The materials were tested for photocatalytic methanol dehydrogenation under simulated solar light (Figure 1). Compared to M_{SA}/UNS and M_{NP}/UNS catalysts, the material containing both SA and NP exhibit higher hydrogen production within 24 hours. This result strongly suggests the presence of a synergistic interaction between the two metallic species, resulting in improved photocatalytic activity.

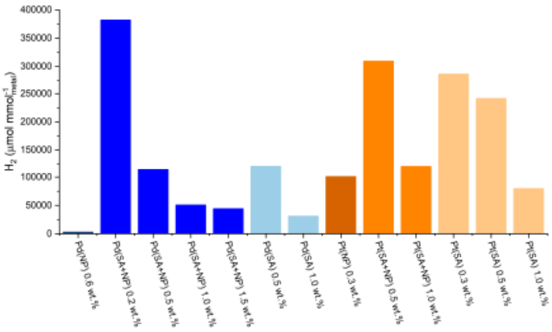


Figure 1*: Photocatalytic H_2 evolution after 24 h of Pt/Pd on UNS under simulated solar.*

Acknowledgements: *the Authors acknowledge the project SAN4FUEL for financial fundings (TWINNING HORIZON-WIDERA-2021-ACCESS-03-01)*

---

[1] C. F. Shih, T. Zhang, J. Li, C. Bai, *Joule*, **2018**, 2, 1925-1949

[2] Z.Gao, T. Montini, J. Mu, N. Luo, E. Fonda, P. Fornasiero, F. Wang, *Journal of the American Chemical Society* **2024**, *146*, 24440-24449

P15: Maleic Anhydride Synthesis through Selective Oxidation Processes: A Comparison of Two Synthetic Strategies

Annamaria Catalano,[1] **Ludovica Conte**,[1] **Marco Brocchi**,[1] **Anna Gagliardi**,[2] **Fabrizio Cavani**,[1]
Tommaso Tabanelli[1]

[1] *Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Italy*
[2] *Polynt S.p.a., Scanzorosciate (BG), Italy*
annamaria.catalano3@unibo.it

Introduction. The synthesis of maleic anhydride (MA) represents a process of great industrial interest, as this anhydride is used to obtain various compounds that find applications in a wide range of fields[1]. Currently, it is mainly produced industrially through the selective oxidation of n-butane, using vanadyl pyrophosphate (VPP) as a catalyst. Global demand for this reagent is expected to grow further in the coming years, while addressing the European and global commitment to adopting increasingly responsible and sustainable practices that are more mindful of environmental and social needs. In this context, the possibility to use butanol, a reagent that can also be obtained from biomass through fermentation, to produce maleic anhydride is being explored. This work focuses on evaluating the catalytic performances of vanadyl pyrophosphate-based catalysts for the synthesis of MA through the oxidation of both 1-butanol and butane.

Experimental. Two catalysts supplied by Polynt S.p.A. were tested: one undoped (A), and the other containing metal promoters as dopants (B). Catalytic performances were evaluated as a function of reaction temperature and contact time, and were assessed in terms of conversion, yield, and selectivity. The catalysts were tested for selective oxidation reactions in continuous fixed bed reactors operating in the gas phase, with an online GC-FID/TCD analysis system for characterizing the main products.

Results and discussion. The tests conducted to synthesize MA from 1-butanol demonstrated that catalyst B is more selective than A: this result is likely due to the positive role played by the metal cations in improving the performance of VPP-based catalysts, promoting the selective oxidation reaction to MA at the expense of total oxidation reactions. The superior catalytic performance of B compared to A is also evident when considering the reactivity of n-butane: the use of the doped catalyst increases the conversion of the alkane and the yield of MA by approximately 10% compared to what is achieved with catalyst A. The productivity calculations (mol/h of MA produced relative to the amount of catalyst introduced into the reactor) also confirm the better performance of catalyst B compared to A in both synthetic strategies. The study conducted by varying the contact time highlighted that for catalyst A, a decrease in contact time leads to an increase in selectivity towards maleic anhydride. This aspect is particularly interesting because it could imply the use of smaller amounts of catalyst to be introduced into the reactor on an industrial scale, with all the economic advantages that such a choice would entail.

---

[1] Chemical Economics Handbook, (2023).

P16: Piers–Rubinsztajn reaction to unlock an 8-step synthesis of 7-hydroxy cannabidiol

Emanuele Cocco,[1] Debora Iapadre,[1] Alessandro Brusa,[1] Pietro Allegrini,[2] Stephen Thomas,[3] Fabio Pesciaioli,[1] Armando Carlone[1,4]

[1] Department of Physical and Chemical Sciences, Università degli Studi dell'Aquila, via Vetoio, L'Aquila, Italy
[2] Indena SpA, viale Ortles, 12, 20139 Milan, Italy
[3] EaStCHEM School of Chemistry, The University of Edinburgh, Edinburgh EH9 3FJ, UK
[4] INSTM, Consorzio Nazionale per la Scienza e Tecnologia dei Materiali, RU L'Aquila, Italy
emanuele.cocco@graduate.univaq.it

Cannabidiol (CBD) is the major nonpsychotropic cannabinoid: it does not produce any of the undesirable psychotropic effects of Δ^9-tetrahydrocannabinol (Δ^9 -THC) and it has shown numerous pharmacological properties such as immunosuppressive and anti-inflammatory actions and can act also as neuroprotective antioxidant.[1] Furthermore, it has shown therapeutic potential in the treatment of some neurological diseases such as epilepsy and psychosis.[2]

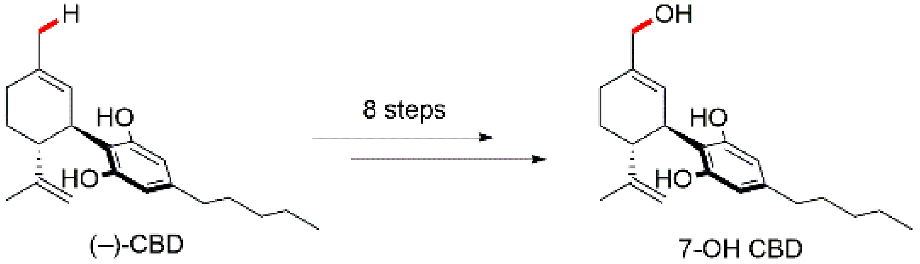
The metabolism of CBD is well established in human species and the first step has been identified as the hydroxylation in position 7, leading to the formation of 7-hydroxy-cannabidiol, followed by further oxidations.[3]

7-OH-CBD has been demonstrated to be an interesting candidate for pharmacological studies but only an eight-steps synthesis from CBD has been proposed until now,[4] which involves a critical step with a neat Grignard reagent at very high temperature.

In this work we propose a new approach towards the artificial preparation of 7-hydroxy-cannabidiol via an eight-step synthesis starting from CBD itself, as represented in Figure 1.

Our approach allowed to complete the synthesis of 7-hydroxy-cannabidiol in eight steps with two telescoped transformations, achieving a 31% overall yield.

The synthesis features an allylic rearrangement and a Piers-Rubinsztajn reaction as key steps,[5,6] this last one allowing the final critical removal of the methyl groups in milder and safer conditions.



✓31% overall yield ✓ mild reaction conditions ✓ Piers-Rubinsztajn reaction to effect a mild deprotection

---

[1] Hampson, A. J.; Grimaldi, M.; Axelrod, J.; Wink, D. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, 95, 8268
[2] Zuardi, A. W.; Morais, S. L.; Guimaraes, F. S.; Mechoulam, R. J. Clin. *Psychiatry* **1995**, 56, 485.
[3] Harvey, D. J.; Samara, E.; Mechoulam, R. Pharmacol. *Biochem. BehaV.* **1991**, 40, 523.
[4] Hanus, L. O.; Tchilibon, S.; Ponde, D. E.; Breuer, A.; Fride, E.; Mechoulam, R. *Org. Biomol. Chem.* **2005**, 3, 1116.
[5] McAulay, K.; Clark, J. S. *Chemistry - A European Journal* **2017**, *23* (41), 9761–9765.
[6] Torrens, A. A.; Ly, A. L.; Fong, D.; Adronov, A. *Eur. J. Org. Chem.* **2022**, *2022* (27).

P17: Ru/Pd catalytic system for the reductive amination of furfural

Matteo Corradini,[1] **Francesca Liuzzi**,[1] **Alessandro Allegri**,[1] **Nikolaos Dimitratos**,[1] **Stefania Albonetti**[1]

[1] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, Italy*
matteo.corradini9@unibo.it

Introduction. In the last decades, supported metal nanoparticles (NPs) have been widely employed for the preparation of high-performance heterogeneous catalysts. Sol-immobilization is an efficient way for the synthesis of such catalysts, allowing the deposition of metal NPs, previously formed in an aqueous solution, on the support's surface[1]. The aim of the present work was to explore the preparation of some ruthenium-based catalysts supported on TiO_2, also evaluating how the activity changes adding Pd in the active phase with various metal:metal ratio. The catalytic performances of the prepared solids have been evaluated in the reductive amination of furfural to furfurylamine.

Results. After an initial study of the influence of various reaction parameters, such as reaction time and temperature, H_2 pressure and ammonia concentration, conducted on ruthenium catalyst, it was possible to identify optimized conditions that allowed achieving a selectivity for furfurylamine around 95%. The effect of various parameters and the results of reactions conducted without a catalyst were then used to delve into the intermediates involved in the process, an investigation that led to the hypothesis of a reaction scheme slightly different from the one usually proposed in the literature regarding the initial species formed (**Scheme 1**). Specifically, it was observed that in the first minutes of the reaction, a trimer of furfurylimine forms, which is then converted to N-furfurylidenefurfurylamine (FDA) and, subsequently, to the primary amine of interest. Finally, to improve the reducing properties of the catalyst, bimetallic Ru/Pd catalysts were prepared, and with small amounts of palladium an improvement in catalytic activity was recorded. However, further increase in the palladium fraction leads to the reduction of the aromatic furan ring.

***Scheme 1**: Proposed reaction scheme for the reductive amination of furfural (FUR) to furfurylamine (FAM).*

---

[1] Monti, E.; Ventimiglia, A.; Forster, L,; Rodriguez-Aguado, E.; Cecilia, J.; Ospitali, F.; Tabanelli, T.; Albonetti, S.; Cavani, F.; Rivalta, I.; D'Agostino, C.; Dimitratos, N. *Green Chem.* **2023**, *25 (7)*, 2640-2652.

P18: Metal-Organic Frameworks as Multifunctional Platforms for MRI-Guided Chemo-Photodynamic Therapy: A Photocatalytic Approach to Cancer Treatment

Nicola Di Nicola,[1] **Roberto Alonzi**,[2] **Mauro Di Vito Nolfi**[3], **Marco Vandone**[4], **Francesco Ferella**[5]
Andrea Lazzarini[1]

[1] Department of Physical and Chemical Sciences (DSFC), University of L'Aquila, Italy
[2] Department of Life, Health and Environmental Sciences (MESVA), University of L'Aquila, Italy
[3] Department of Biotechnological and Applied Clinical Sciences (DISCAB), University of L'Aquila, Italy
[4] Department of Chemistry, University of Milano, Italy
[5] Gran Sasso National Laboratories (INFN), Italy
nicola.dinicola@graduate.univaq.it

Metal-Organic Frameworks (MOFs) are porous crystalline materials composed of metal clusters connected by organic binders, known for their structural adaptability and wide range of applications[1]. While extensively used in sensing, catalysis, and gas adsorption, their biomedical potential is limited by concerns over ligand toxicity and metal accumulation. Recent advances highlight MOFs' unique properties, such as favorable dimensions and tumor-targeting capabilities, which make them promising for cancer theranostics. A notable application is photodynamic therapy (PDT), where porphyrin linkers in MOFs act as photosensitizers. Upon light activation, these linkers generate reactive oxygen species (ROS) to selectively destroy tumor cells. Additionally, some MOFs enhance theranostic potential through catalytic reactions involving glucose or hydrogen peroxide.

MOFs' high loading capacity allows them to carry contrast agents, anticancer drugs, and photosensitizers, enabling integrated cancer diagnosis and treatment[2]. This study focuses on the PCN-224 system as a carrier of MRI contrast agents, specifically chelating Gd^{3+} or Mn^{2+} ions within the porphyrin ring. Chelation reduces metal leaching, minimizing risks while enhancing therapeutic efficacy. The porphyrin also contributes to therapies such as PDT, chemotherapy, and neutron capture therapy (NCT)[3]. The Gd-PCN-224 system combines MRI imaging with chemo-photodynamic therapy, offering a versatile tool for precise tumor destruction and advanced imaging.

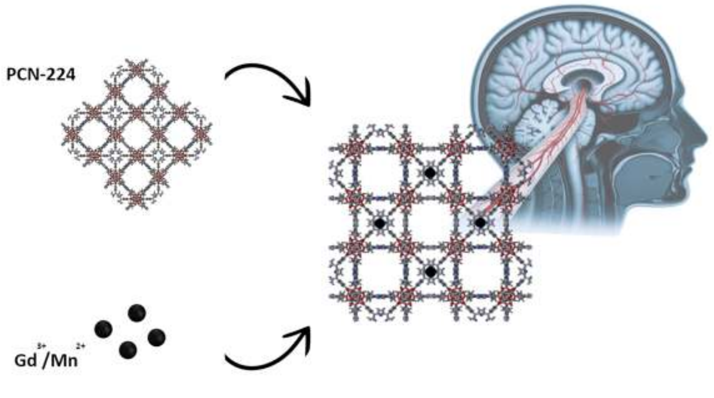


Figure 2*: schematic representation of the loading process and application of the Gd/Mn@PCN-224 system*

---

[1] Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* ***2013***, *341*, 1230444.

[2] Lázaro, I. A.; Forgan, R. S. Coordination Chemistry Reviews **2019,** *380,* 230–259.

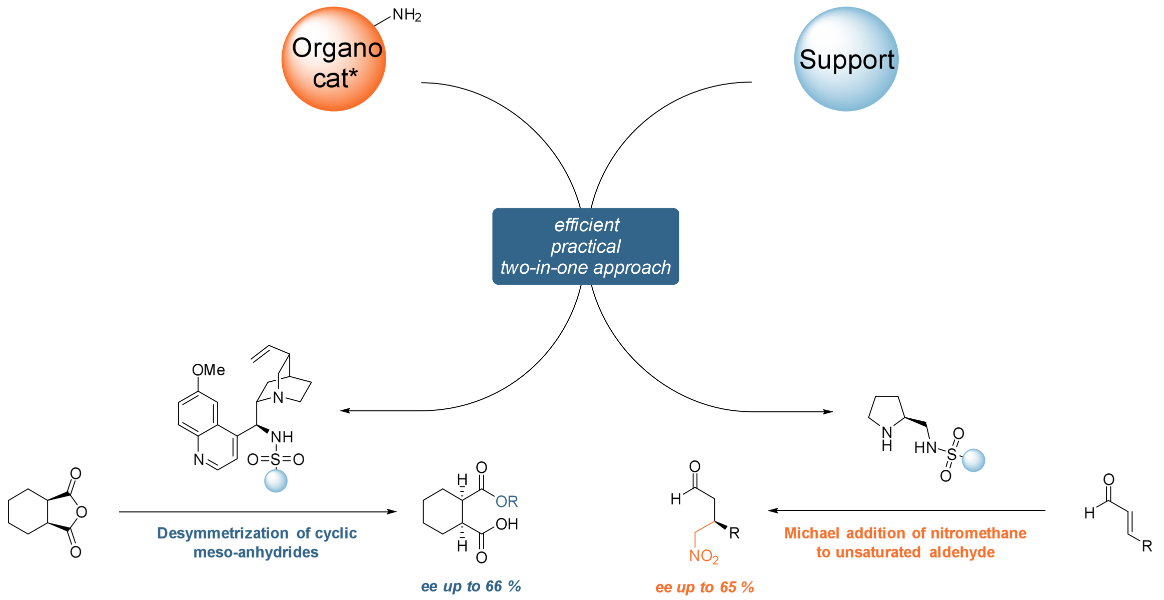
[3] Kim, S.; Yang, J. U.; Ahn, J. H.; Ko, I. O.; Kim, J. Y.; Lee, Y. J.; Park, J. A . ACS Med. Chem. Lett. **2021**, *12*, 1459−1463.

P19: Combining immobilization and catalytic site formation for heterogeneous organocatalysis

Matteo Di Saverio,[1] **Armando Carlone**,[1,2] **Fabio Pesciaioli**[1]

[1] *Department of Physical and Chemical Sciences, Università degli Studi dell'Aquila, 67100 L'Aquila, Italy*
[2] *INSTM, Consorzio Nazionale per la Scienza e Tecnologia dei Materiali, 67100 L'Aquila, Italy*
matteo.disaverio@student.univaq.it

Homogeneous organocatalysis has unlocked new frontiers; nevertheless, there are several reasons to support the immobilization of organic catalysts. Among the most important are the simplified separation of the catalyst from the reaction mixture, the easier isolation of reaction products, and the recovery and recycling of the catalyst. Catalyst instability may also justify immobilization. Some organic catalysts tend to gradually decompose under the reaction conditions, releasing trace by-products that require separation from the desired products. Immobilization becomes particularly advantageous when the catalyst is costly, results from a complex synthesis process, or is required in relatively large quantities.[1] In most cases, immobilization involves one or more additional synthetic steps necessary for the process and for generating functional groups that can be used to bind the catalyst to the support. These additional steps often result in higher costs.[2] To address this issue, we propose an immobilization strategy which allows to form simultaneously a bond between the catalyst and the support while generating a sulfonamide group, a common and versatile organocatalytic active site, used as catalytic site.[3] Following this strategy, we have synthesized and characterized several heterogeneous chiral organocatalysts, which were then evaluated for their activity in asymmetric catalysis.



---

[1] Cozzi F., *Adv. Synth. Catal.* **2006**, *348* (12-13), 1367-1390.
[2] Rodríguez-Escrich, C., *Catalyst Immobilization: Methods and Applications* **2020**, Wiley-VCH, Weinheim, 217-256.
[3] Giorgianni G., Casacchia M., Ricci P., Di Muzio S., Lazzarini A., Carlone A., Pesciaioli F., *Synlett* **2024**, *35*. https://doi.org/10.1055/a-2349-1863.

P20: HETEROGENEOUS CATALYTIC SYSTEMS AS VERSATILE TOOLS FOR THE SAFE AND SUSTAINABLE DECONTAMINATION OF HAZARDOUS CHEMICAL AGENTS

<u>Stefano Econdi</u>,[1] **Matteo Guidotti,**[1] **Chiara Bisio**[2]**, Fabio Carniato**[2]**, Stefano Marchesi**[2]

[1] *CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", Milan, Italy*
[2] *DISIT, University of Eastern Piedmont "Amedeo Avogadro", Alessandria, Italy*
stefano.econdi@scitec.cnr.it

Decontamination is a critical and essential capability to mitigate, and in the best cases, neutralize the threat posed by hazardous chemicals to human health and the environment. For this reason, the transition from traditional stoichiometric methods to catalytic approaches plays a key role in achieving effective and sustainable decontamination of these substances[1]. In this scenario, a synthetic saponite clay containing structural Nb(V) metal centers (NbSAP) was investigated for the liquid-phase degradation of paraoxon-ethyl, an anti-cholinergic organophosphorus obsolete agrochemical and nerve warfare agent simulant, under mild ambient conditions. More than 80 % of the initial concentration of paraoxon-ethyl was converted in less than 30 min into non-noxious products thanks to a cooperative acid-catalysed degradation, alkaline hydrolysis and, to a lesser extent, adsorption of the substrate. Such promising activity is attributed to the high density of Brønsted acid sites, obtained through the tailored inclusion of Nb(V) species in the solid framework, and the co-presence of Na^+ species introduced at the exchangeable sites along with the pristine synthesis gel. Furthermore, NbSAP showed excellent regeneration capability, retaining its ability to degrade the pollutant after three catalytic cycles[2]. Likewise, cation exchange resins with strong acid sulfonic groups, were selected and studied for the catalytic oxidative degradation of (2-chloroethyl)ethyl sulfide (CEES), a chemical warfare agent (CWA) simulant of the blistering sulfur mustard, in the presence of aqueous H_2O_2. The synergistic interaction between the resin's Brønsted acid sites and the oxidizing species led to the complete conversion of CEES in few hours, with a gradual formation of the corresponding non-toxic sulfoxide (CEESO), followed by a slower reaction to the toxic sulfone ($CEESO_2$). This system thus proved to be effective in the chlorine-free oxidative abatement of organosulfur hazardous agents, even after four consecutive catalytic cycles. These studies lay the foundation for efficient, sustainable and versatile decontamination methods, suggesting potential applications in catalytic fixed beds for depollution of effluents or as films for self-cleaning surfaces in chemical-contaminated environments.

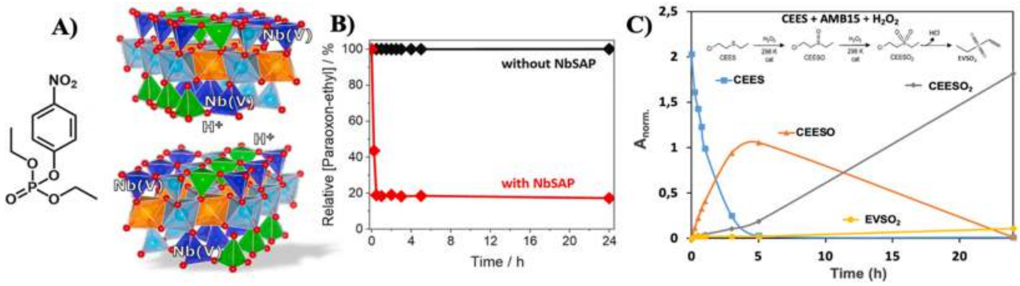


Figure 1: A) Schematic sketch of NbSAP clay; B) Concentration profiles of paraoxon-ethyl vs. time in the presence/absence of NbSAP; C) CEES degradation reaction profile vs. time over Amberlyst15 in presence of aq. H_2O_2.

Acknowledgements: *S.E. thanks GIC for support to attend the GIC-EFCATS Winter School of Catalysis through a scholarship*

---

[1] S. Econdi, A. Caselli, S. Marchesi, F. Carniato, C. Bisio, M. Guidotti, *Eur. Phys. J. Plus* **2024**, *139*, 782.
[2] S. Marchesi *et al.*, *Heliyon* **2024**, 10, 21, e39898.

P21: Rheological study of iron molybdate catalyst

Giorgia Ferraro,[1] N. Ballarini,[2] M. Signoretto[1]

[1] Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RUVe Via Torino 155, 30172-Venice, Italy

[2] Clariant, Via Fauser 36, 28100 Novara, Italy

giorgia.ferraro@unive.it

Formaldehyde is a versatile chemical widely used in the production of resins, disinfectants, and various organic compounds.[1] Its global demand has grown significantly, with over 70% of production relying on iron-molybdenum oxide catalyst due to its efficiency and lower operating costs compared to the silver catalyst.[2] Despite its advantages, the iron-molybdenum catalyst preparation step faces some challenges, including temperature sensitivity, the transport of highly viscous liquid, and stability issues, which can affect industrial efficiency. To overcome this technical issue and to improve catalyst performance, this study, conducted in collaboration with Clariant, aims to enhance catalyst stability, reduce the wastes, and minimize the production costs.[3] To do this, rheological analyses of the paste-like catalyst were performed, involving rotational and oscillatory tests to evaluate viscosity, yield points, and deformation behavior under different conditions of water content and temperature. The catalyst exhibited both pseudoplastic and thixotropic behaviors, indicating structural breakdown and recovery under shear stress, while oscillation tests revealed viscoelastic properties, with the material transitioning from solid-like to liquid-like behavior with increasing shear. These findings provide insights into the structural stability and flow properties of the catalyst, crucial for optimizing its synthesis and performance. This research contributes to improving operational efficiency and supports the broader goals of industrial and environmental sustainability.

Figure 1*: Scheme of catalyst preparation*

---

[1] K. Shakeel *et al*., *Processes* **2020**, *8*, 571.

[2] H. I Mahdi *et al*, *Mol. Catal.* **2023**, *537*, 112944.

[3] Decarbonization and Circular Economy. https://www.clariant.com/en/Business-Units/Catalysts/Decarbonization-and-Circular-Economy.

P22: Ceria-Based Catalysts for the Direct Conversion of CO_2 to Dimethylcarbonate

<u>Gionata Galliano</u>[1], Sadaf Fatima Jafri[1], Edoardo Bracciotti[1], Luca Braglia[2], Andrea Jouve[1], Sergio Rojas-Buzo[1], Silvia Bordiga[1], Elisa Borfecchia[1]

[1]Department of Chemistry, NIS Center and INSTM Reference Center, University of Turin, 10125 Turin, Italy
[2]AREA Science Park, Padriciano 99, Trieste, I-34149 Italy
gionata.galliano@unito.it

Carbon dioxide (CO_2), a major greenhouse gas, is also a sustainable feedstock for valuable chemicals like dimethyl carbonate (DMC), used in methylation, polycarbonate synthesis, and as a fuel additive. Direct DMC synthesis from CO_2 and methanol offers a promising, eco-friendly solution to reduce emissions and enable industrial applications [1]. In this regard, Ce-based catalysts are widely known for their redox properties in various catalytic reactions, such as CO_2 methanation (CM) and CO_2 conversion to DMC [2]. The presence of oxygen vacancies on the CeO_2 catalyst surface can favor the CO_2 activation, being reactive sites and the key components of oxygen storage in oxidation reaction [3]. To understand and enhance the catalytic performances of CeO_2 for the direct conversion of CO_2 to DMC, oxidation state, Ce^{3+}-V_O and surface defectivity need to be studied. In this work, we investigated CeO_2 based catalysts under reaction conditions. The catalysts were obtained with different synthetic routes, including a novel approach through the calcination of Ce-MOF materials [4]. The Ce^{3+}/Ce^{4+} redox properties are investigated by Ce $M_{4,5}$-edge Near edge X-ray absorption fine structure (NEXAFS) spectroscopy [5] collected at the APE-HE NEXAFS beamline at the Elettra synchrotron. Multivariate Curve Resolution (MCR) facilitated extracting underlying chemical information about Ce^{3+} and Ce^{4+} spectral pure components and their concentration evolution during catalysis. Furthermore, FT-IR spectroscopy was used to monitor each step of the adsorption and the formation of the intermediates and products on the catalyst surface. Finally, the catalytic efficiency of the cerium oxides was assessed by determining the DMC yield from the reaction between CO_2 and methanol. This study is a crucial contribution to the development of a more efficient catalyst for the production of DMC from CO_2

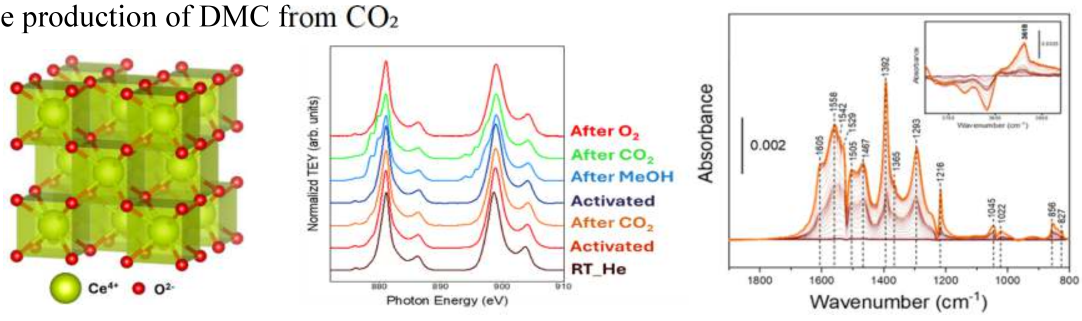


Figure 1. ***(left)*** *CeO_2 fluorite face centered cubic structure obtained using the VESTA software* ***(middle)*** *Evolution of the Ce $M_{4,5}$-edges NEXAFS spectra of CeO_2 catalyst obtained at selected key steps following the experimental protocol.* ***(right)*** *In situ difference IR spectra collected during CO_2 adsorption*

---

[1] K. Xuan et al.*Journal of CO2 Utilization*,**2018**,*27*,272-282
[2] A. H. Tamboli et al., *Chem. Eng. J.*, **2017**, 323, 530-544.
[3] B. Liu et al., *ACS Catal.*, **2018**, 8, 10446–10456.
[4] S. Rojas-Buzo et al., *Appl. Catal. B*, **2024**, 346, 123723
[5] D. Salusso et al., *Nanomaterials*, **2023**, 13, 272.

P23: HYDROGEN PRODUCTION BY PHOTOREFORMING USING COMPOSITES BETWEEN TiO_2 AND Nb_2O_5 AS PHOTOCATALYSTS.

Alberta Genco,[1,2] **Elisa I. García-López,**[3] **Narimene Aoun,**[1] **Bartolo Megna,**[1] **Conchi O. Ania,**[4] **Giuseppe Marcì**[1]

[1]*Department of Engineering (DI), Viale delle Scienze, University of Palermo, Palermo, Italy*
[2]*Department of Chemistry, University of Perugia, Perugia, Italy*
[3]*Department of Chemistry (STEBICEF) University of Palermo, Italy (elisaisabel.garcialopez@unipa.it)*
[4]*POR2E Group, CEMHTI CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France*
alberta.genco@dottorandi.unipg.it

Photoreforming for H_2 production, coupled with oxidative processes in the presence of a semiconductor, is a promising method for generating both H_2 and high-value chemicals[1]. Nb_2O_5 has been investigated as a photocatalyst due to its properties as good chemical stability, non-toxicity, and commercial availability. Its valence and conduction band levels are well-positioned for H_2 production.[2] Constructing heterostructures with Nb_2O_5 and other TiO_2 offers a way to boost the photocatalytic performance of the oxide, providing benefits like enhanced light absorption in the visible spectrum, improved charge separation.[3] The addition of Pt as a co-catalyst further enhances the H_2 productivity. Alcohols acts as hole scavengers for H_2 generation, because it has been reported that the most efficient substrates for photoreforming must contain an oxygenated functional group and a hydrogen atom in the "α" position.[4] Nb_2O_5 was prepared by using ammonium niobium oxalate (ANbO) as the precursor. The choice of the precursor strongly influences the physical-chemical features and hence the performance of the photocatalyst, and consequently analogous materials obtained from $NbCl_5$[3] were also tested for the sake of comparison. The photocatalysts obtained from ANbO were synthesized hydrothermally, and the preparation time was varied from one to four days to study its influence on the chemical-physical properties and photocatalytic activity of the materials. An analogous procedure was carried out to prepare Nb_2O_5-TiO_2 composites with a Nb_2O_5 : TiO_2 ratio of 1 : 10 w/w. TiO_2 Evonik P25 was suspended in the ANbO solution and the suspension was hydrothermally treated at 175 °C.

Photo-reforming tests were performed both under UV and natural solar irradiation and the effect of Pt (1 % w/w) was studied as further co-catalyst. Sample Nb3 prepared after three days of hydrothermal treatment displayed the highest total amount of H_2 produced, in particular the Nb_2O_5-TiO_2 composites materials resulted more active with respect to the pristine niobia. In particular, the composite material prepared maintaining the precursors for 3 days under hydrothermal conditions (Nb-Ti-3) was the most active sample for which the H_2 formation under UV irradiation resulted of ca. 138 $mmol \cdot h^{-1} \cdot g^{-1}$ with an apparent quantum efficiency (AQE) of ca. 37 %. Whereas the productivity of H_2 of the same photocatalyst under natural sunlight irradiation was 40 $mmol \cdot kJ^{-1} \cdot g^{-1}$ and the AQE reached a value of 85 %. All the powders have been fully physico-chemically characterized.

References

[1] E.I. García-López, L. Palmisano, G. Marcì, ChemEng.7 (2023) 11
[2] C. Avcıoglu, S. Avcıoglu, M. F. Bekheet, A. Gurlo, Materials Today Energy 24 (2022) 100936
[3] E.I. García-López, A. Genco, V. Lagostina, M.C. Paganini, G. Marcì. Catal. Today 423 (2023) 114283.
[4] M. Bowker, C. O'Rourke, A. Mills, Top. Curr. Chem. 380 (2022) 17.

P24: CHARACTERIZATION OF MATERIALS FOR CH_4 CAPTURE IN CATTLE BARNS

<u>Alice Gramegna</u>,[1,2] **Matteo Tommasi,**[1,2] **Simge Naz Degerli,**[2] **Ilenia Rossetti,**[1,2]

[1] Department of Chemistry, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milan, Italy
[2] INSTM Unit Milano-Università, Via C. Golgi 19, 20133 Milan, Italy
alice.gramegna@unimi.it

In 2022, ruminants, mainly dairy cattle accounted for about 78 % of the total agricultural methane emission in Europe [1]. Given the growing cattle population resulting from intensive farming, capturing and valorizing the greenhouse gases produced has become crucial. This work examines a novel approach based on gas adsorption over selected adsorbent materials. During our research, we identified two major challenges: capturing methane at low partial pressures and competitive adsorption due to higher CO_2 and H_2O vapor concentration in cattle barns. These aspects require selecting adsorbent materials with properties that enhance CH_4 uptake. Considering the physisorption nature of the process, the structural properties of the material play a crucial role. Comprehensive characterization of three different activated carbon (Actisorb 70, Actisorb 100 and Suracsh) was performed using SEM-EDX, XRD and BET analysis. According to these, Actisorb 70 exhibited the most favorable properties, featuring an amorphous structure along with the highest SSA, total pore volume, and pore width. The adsorption capacity of all samples was evaluated using TGA and TPD-MS analysis after exposing the materials in a real cattle stable at different location and for different exposure times. Actisorb 70 displayed the most promising results among the activated carbons, confirming the importance of structural properties in adsorption. In particular, comparing the TGA of the sample with that of the blank revealed clear adsorption, which TPD-MS analysis identified as methane and carbon dioxide adsorption, in Fig. 1, beside water and some minor gases. Actisorb 70 has shown encouraging adsorption capabilities, making it a potential candidate for GHGs capture in cattle stable.

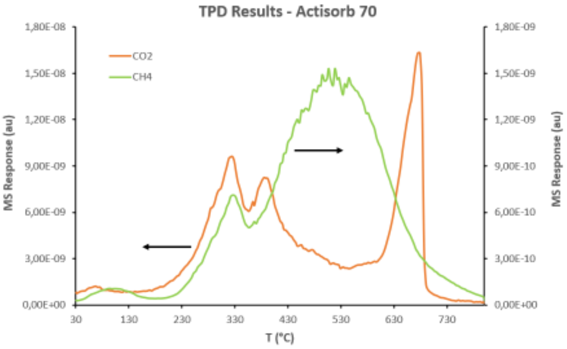


Figure X: *TPD-MS analysis results of Actisorb 70*

Acknowledgements: *This study was carried out within the Agritech National Research Center and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022).*

---

[1] EEA - European Environment Agency.” 2024. 2024. https://www.eea.europa.eu/en/analysis/maps-and-charts/greenhouse-gases-viewer-data-viewers?activeTab=8a280073-bf94-4717-b3e2-1374b57ca99d.

P25: Lignin valorization for biofuel and chemicals production

Peyman Hamidizadeh[1], **Maria Michela Dell'Anna**[1], **Piero Mastrorilli**[1], **Isabella De Bari**[2]

[1] *DICATECh, Politecnico di Bari, via Orabona, 4, I-70125 Bari, Italy1*
[2] *ENEA, Trisaia Research Center, SS 106 Ionica, km 419+500, 75026 Rotondella (MT), Italy*

p.hamidizadh@phd.poliba.it

Lignin, a key component of plant biomass, has great potential as a sustainable resource for bioenergy and bioproducts. Its abundance and renewability make it a promising alternative to fossil fuels.[1]
Deep Eutectic Solvents (DES) are effective green solvents for breaking down lignin, facilitating its conversion into valuable chemicals.[2] Additionally, nickel-based catalysts, such as Raney-Nickel, are highly effective in depolymerizing lignin, especially in electrocatalytic hydrogenolysis, making the process more efficient and sustainable.[3]
This study demonstrates that the hydrogenation of lignin using Nickel Raney catalyst is highly dependent on the reaction conditions. The optimal conditions were identified, providing the highest yield and selectivity of depolymerized products. While the oil production percentage remained stable between methanol and ethanol, using higher amounts of Nickel Raney led to the formation of eicosane, demonstrating the potential for producing alkanes. Raising the reaction temperature decreased the amount of phenolic compounds but increased the production of esters and aromatic compounds. These findings offer valuable insights for efficiently converting lignin into valuable chemical feedstocks, contributing to the development of sustainable biomass utilization strategies.

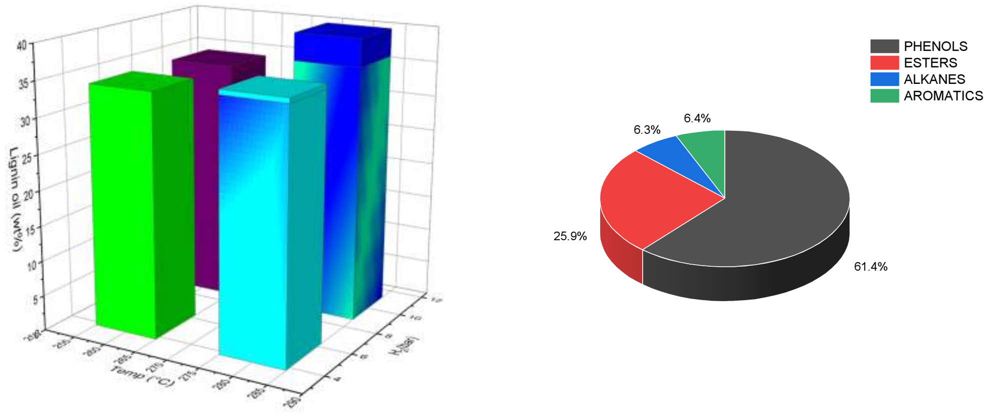


Figure 1: *A) Lignin oil yield conversion in the presence of different amounts of Raney-Nickel, 80 and 200 mg. All reactions proceeded for 4 hours. B) Product distribution*

Acknowledgments: *We appreciate the support of the ENEA Research Institute for providing funding(fellowship) and resources.*

[1] Chio, C.; Sain, M.; Qin, W. *Elsevier Ltd June 1*, (**2019**),232–249.
[2] Colella, M.; Romanazzi, G.; Petrelli, V.; Baldassarre, F.; Ciccarella, G.; Catauro, M.; Mastrorilli, P.; Dell’Anna, M. M. *Macromol Symp* (**2022**), 404 (1).
[1] Morgana, M.; Viola, E.; Zimbardi, F.; Cerone, N.; Romanelli, A.; Valerio, V. *Processes* (**2021**), 9 (7).

P26: Valorization of Orange Peel Waste to viable chemical intermediate products via diluted acid hydrolysis

Ali Hussein Hammoud,[1,2] Prof. Francesco Mauriello,[2] Dr. Emila Paone,[2] Dr. Majd Al-Naji [1]

[1]BasCat- UniCat BASF JointLab, Technische Universität Berlin, Germany
[2] DECHEMA, Dipartaminto Ingeneria, Università degli Studi Mediterranea di Reggio Calabria, Italy

hammoud@campus.tu-berlin.de

Citrus fruits, particularly oranges, are among the most widely cultivated fruits globally, with orange production concentrated in the Mediterranean region, particularly in Spain and southern Italy [1,2]. Despite their economic significance, the orange juice industry generates substantial quantities of orange peel waste (OPW), comprising approximately 50% of the processed fruit [3]. OPW contains valuable components such as lignocellulose, pectin, and D-limonene, but traditional valorization methods like landfilling and animal feed raise environmental concerns due to methane emissions, CO_2 release, and soil contamination. Consequently, valorization strategies for OPW, such as essential oil extraction and lignocellulosic hydrolysis, have gained traction[1,3].

This study investigates dilute, two stage acid hydrolysis of OPW for the production of fermentable sugars, focusing on optimizing reaction parameters and scaling the process for industrial feasibility. Pure cellulose and hemicellulose hydrolysis were systematically analyzed using various acid catalysts, concentrations (1, 3 and 6 wt%), pretreatment methode as well as varrying reaction duration (up to 300 min) and temperature, both in laboratory (50 ml) and scaled-up (5 l) glass batch reactors. Hydrochloric acid (6 wt% HCl) was identified as the most effective catalyst for cellulose conversion at 100°C, achieving high conversion, while maintaining high glucose selectivity compared to other acid catalysts. Ball milling pretreatment significantly enhanced hydrolysis by reducing cellulose crystallinity, achieving a 16% improvement in conversion compared to untreated cellulose.

Hemicellulose hydrolysis demonstrated superior xylose yields with HCl alongside formic acid, while formic acid was selected for OPW hydrolysis due to its lower corrosivity, reusability, and greener profile. The addition of NaCl and $AlCl_3$ as co-catalysts was evaluated, revealing their complex roles in enhancing conversion but also promoting sugar degradation under specific conditions.

The hydrolysis of orange peel waste (OPW) and fresh orange peel (FOP) was conducted under optimized two-stage conditions. Stage 1 involved 6 wt% formic acid, supplemented with 0 or 10 wt% NaCl, while Stage 2 employed 6 wt% hydrochloric acid (HCl), with reaction temperatures ranging from 70 to 100°C. Results demonstrated the selective hydrolysis of hemicellulose during Stage 1. However, the higher soluble sugar content in OPW, attributed to prior juice extraction, led to sugar degradation and humin formation during prolonged reactions, particularly in Stage 2 with 6 wt% HCl. Ongoing scaling studies are extending the process to reactors up to 5 liters, with the aim of developing a sustainable and industrially viable method for OPW valorization.

---

[1] O.S. Mariana, C. Alzate, and C. Ariel, *Journal of Cleaner Production* 2021, **322**, 128814

[2] S. Consoli, C. Caggia, N. Russo, C.L. Randazzo, A. Continella, G. Modica, S.O. Cacciola, L. Faino, M. Reverberi, A. Baglieri, I. Puglisi, M. Milani, G. Longo Minnolo, and S. Barbagallo, *Sustainability (Switzerland)* 2023, **15** (3), 2482

[3] Á. Siles López, J. Li, and I.P. Thompson, *Critical Reviews in Biotechnology* 2010, **30** (1), 63–69

P27: Investigating the benefits of flow systems to improve inline analysis of biocatalytic reactions

S. Helin,[1] **K. A. Vincent**,[1]

[1] *University of Oxford, United Kingdom*
sofia.helin@linacre.ox.ac.uk

Flow chemistry is revolutionising the future of synthesis, by providing inline monitoring opportunities and a small volume for the reaction to occur, which means greater local catalyst concentration and improved efficiency.[1] Biocatalysis using renewable feedstocks such as H_2 improves the sustainability of traditional hydrogenation reactions,[2] by enabling reactions at milder conditions with green solvents.

Previous work[3] has involved using NADH as a cofactor (£133 g^{-1})[4] for cofactor recycling and investigated the use of other flavins[5] and this work investigates flavin mononucleotide (FMN, £10 g^{-1})[6] reduction in flow to test the feasibility of the cofactor recycling system in flow.

In this work I will explore the different flow systems tested, with a test reaction of flavin-mononucleotide reduction by a hydrogenase enzyme, which will be used as a flavin recycling system with a secondary enzyme in future. The FMN reduction can be monitored with inline UV-vis, as the oxidised FMN is yellow with a strong absorbance at 445nm. Important criteria of the flow system include: ability to monitor oxygen sensitive intermediates, good gas/liquid mixing, cost-effectiveness and stability.

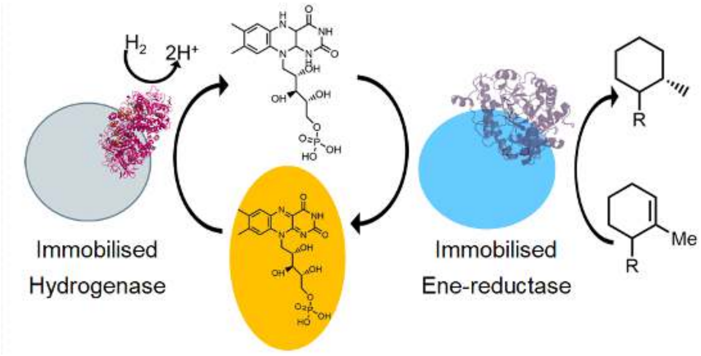


Figure 1: *Reaction scheme to show the full enzyme cascade of the ene-reductase coupled to the Hyd1 hydrogenase and riboflavin (RF) cofactor recycling.*

---

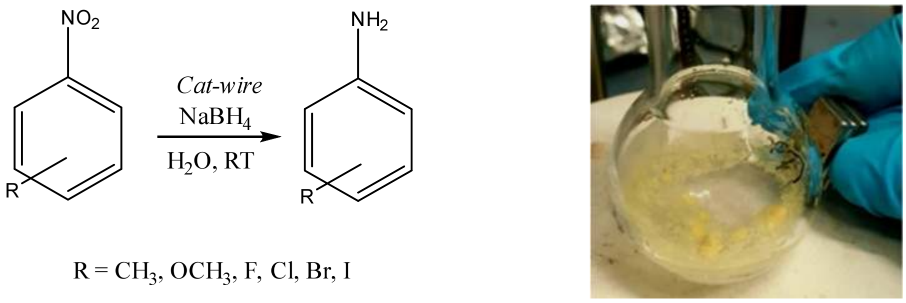
[1] Plutschack, M. B.; Pieber, B.; Gilmore, K.; Seeberger, P. H., *Chemistry Review,* **2017**, *117* (18), 11796–11893.
[2] Drelinkiewicza, A.; Waksmundzka, A.; Makowski, W.; Sobczak, J. W.; Król, A.; Zie¸ba, *Catalysis Letters,* **2004**, *94 (3/4)*, 143–156.
[3] A. Reeve, H.; Lauterbach, L.; A. Ash, P.; Lenz, O.; A. Vincent, K. A, *Chemical Communications,* **2012**, *48 (10)*, 1589–1591.
[4] NAD Grade I, free acid 53-84-9. http://www.sigmaaldrich.com/ (accessed 2024-11-24).
[5] Joseph Srinivasan, S.; Cleary, S. E.; Ramirez, M. A.; Reeve, H. A.; Paul, C. E.; Vincent, K. A., *Angewandte Chemie,* **2021**, 133 (25), 13943–13947.
[6] Flavin mononucleotide | Sigma-Aldrich. (accessed 2024-11-20).

P28: A SECOND LIFE FOR E-WASTE: A CATALYST FROM DISCARDED CAPACITORS ACTIVE IN HYDROGENATION REACTION OF NITROARENES

Alessia Iennaco,[1] **Francesca Derobertis[1], Piero Mastrorilli[1], Angelo Nacci[2], Maria Michela Dell'Anna[1], Antonio Monopoli[2]**

[1]*DICATECh, Politecnico di Bari, Italy;*
[2]*Dipartimento di Chimica, Università degli studi di Bari "Aldo Moro", Italy*
a.iennaco@phd.poliba.it

The aim of this study is to employ waste derived from electrical and electronic equipment (WEEE), such as capacitors from discarded printed circuit board (PCB), as catalysts in fine chemical reactions. The amount of electronic waste (e-waste) generated worldwide is constantly rising [1]. This type of waste contains potentially toxic and polluting substances, which pose a threat to human health and the environment [2]. On the other hand, if properly managed, they become valuable resources thanks to their high content of critical raw materials (CRM) [1]. In this work the WEEE were initially ground to obtain a fine powder and some needles with a size less than 1 mm. Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray Analysis (EDX) and Thermogravimetric analysis (TGA) of the milled samples revealed the presence of potentially catalytic metals (Cu and Fe) [3] and plastic polymers. TGA results also allowed us to choose the suitable temperature for calcining the materials, carried out to eliminate the organic phase (plastic). The reductions of nitroarenes to their corresponding amines were selected as a class of reactions to test the catalytic activity of the materials (cat-wire and cat-powder) obtained from multilayer ceramic capacitors. As bench reaction we used hydrogenation of nitrobenzene to aniline in water, at room temperature, with $NaBH_4$ as reducing agents. The magnetic catalyst, cat-wire, could be easily separated from the reaction mixture and recycled up to six times. Cat-wire was also active in the reduction of other substituted nitro compounds.



R = CH_3, OCH_3, F, Cl, Br, I

Figure 1*: Hydrogenation reaction of nitroarenes catalyzed by cat – wire and magnetic separation of cat-wire from mixture reaction*

[1] C.P. Baldé, *Global E-waste Monitor*, **2024**, https://ewastemonitor.info/the-global-e-waste-monitor-2024/
[2] K. Brindhadevi, *Environ Res*, **2023**, *217*, 114926
[3] Formenti D., *Chemical rev*, **2019**, *119*, 2611-2680

P29: Green and Cost-Efficient Synthesis of Glycerol Carbonate Derivatives *via* Continuous Manufacturing and Purification Process

Mert Can Ince,[1] and Gianvito Vilé[1]

[1] *Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Italy*
Presenting author: mertcan.ince@polimi.it

Continuous-flow manufacturing of active pharmaceutical ingredients (APIs) is an innovative approach in chemical production *via* utilizing microreactors (e.g., coil and chip reactors).[1] The technique offers strategies to overcome prolonged reaction durations, severe operating conditions and formation of unstable intermediates while exhibiting higher yields and enhanced green metrics with respect to batch manufacturing method.[2] As the reliance on microreactors increases due to their respective benefits, it is essential to facilitate the integration of upstream and downstream processes to establish a continuous and efficient operational system. Despite recent developments, a comprehensive study of an integrated continuous synthesis and purification process combined with an in-depth comparative assessment of techno-economic metrics and life-cycle impacts is still missing in the literature. To address this gap, we have developed a continuous-flow and purification system utilizing a coil reactor and multi-column counter-current solvent gradient purification (MCSGP) process for mephenesin, an active pharmaceutical ingredient (API) prevalently used as a muscle relaxant that has not previously been adapted for continuous-flow synthesis in the literature. The initial batch studies exhibited that optimization parameters such as catalyst type, temperature, reaction time, reagent equivalence, and catalyst amount resulted in a performance that outperformed literature reported values, achieving a 65% yield within 4 hours. Moreover, the protocol was successfully applied to the continuous-flow approach demonstrating the method's broad applicability and versatility with its intrinsic properties. In addition, the first stage of the in-line multi-column purification process was completed by obtaining the Henry adsorption constants for each component of the reaction in order to further use in the automatized MCSGP process. It was examined that in comparison between the adsorption constants of mephenesin, DPP and o-cresol components with respect to the same mobile phase polarity (Acetonitrile/H_2O), DPP retained more on the non-polar stationary phase by far while o-cresol eluted rapidly in contrast. Furthermore, the effect of mobile phase polarity was investigated towards the less polar mobile phase of 10% ACN/H_2O, as a result, it was demonstrated that the separation process of the reaction components was successfully achievable.

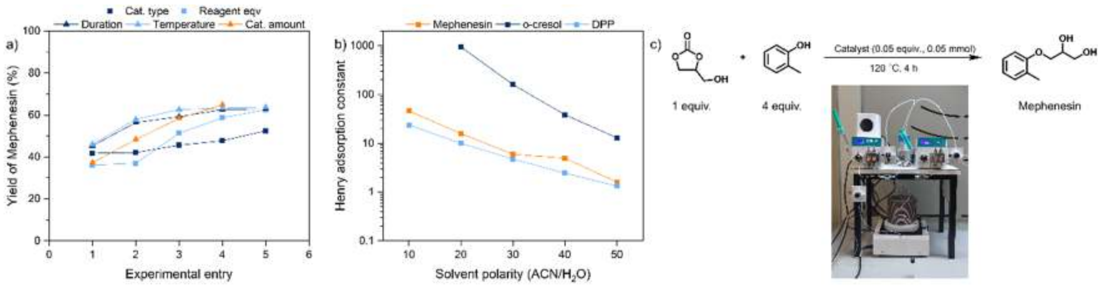


***Figure 1**: Optimization of operating conditions for batch synthesis (a), Henry adsorption constants for mephenesin, o-cresol and DPP (b), reaction scheme with the continuous-flow reactor setup (c).*

---

[1] C. A. Hone, C. O. Kappe, *Chemistry - Methods* **2021**, *1*, 454-467.

[2] A. Sivo, I. Montanari, M. C. Ince and G. Vilé, *Green Chem.*, **2024,** 26, 7911-7918.

P30: NEW HYDROGEN BONDING MOTIFS FOR ANION BINDING CATALYSIS

Alessio Carioscia, Debora Iapadre, Elena Incerto, Jonathan Di Pietro, Fabio Pesciaioli*, Armando Carlone*

Università degli Studi dell'Aquila
elena.incerto@student.univaq.it

Inspired by nature, supramolecular catalysis exploits non-covalent interactions to accelerate chemical transformations [1]. Indeed, weak bond interactions have attracted great interest and in particular anionic bond plays an important role in the field of catalysis [2]. This type of catalysis can be accomplished using H-bonding, as well as halogen bonding, and chalcogen bonding. In each case, the binding of an anion is pivotal to promoting a chemical reaction in which ionic or ionizable substrates could be susceptible to nucleophilic attack. In this context, we aim to study the properties and catalytic performance of carbazole-triazoles, acting as receptors for anion based on 1,8-diaminocarbazole scaffold, which is well known for its anion-binding abilities [3]. A family of structurally related diaminocarbazole receptors has been prepared using a convergent, robust and high-yielding synthesis; their anion-binding properties have been evaluated in terms of binding constants toward different anions and catalytic activity has been tested in a benchmark reaction.

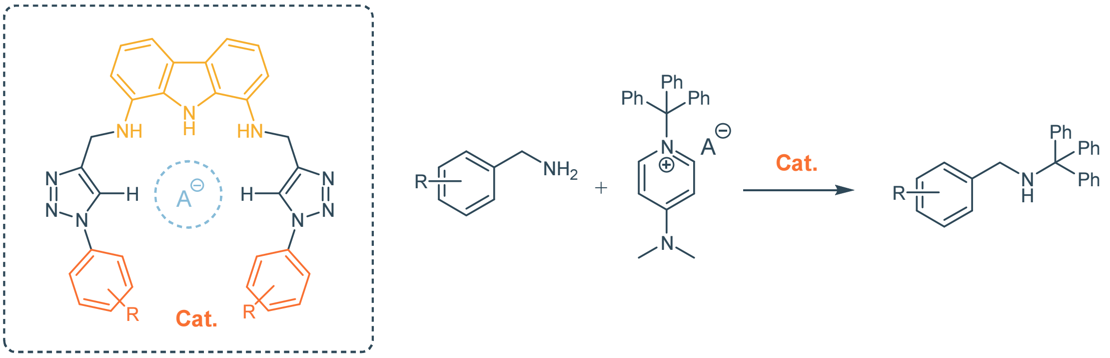


***Figure 1**: General structure of the receptors based on a 1,8-diaminocarbazole scaffold and catalytic system explored using them as a catalyst.*

---

[1] R. Breslow; S. D. Dong, Chem. Rev. 98 (1998) 5, 1997-2012
[2] J. M. Ovian, P. Vojá čková, E. N. Jacobsen, *Nature* 616 (2023) 84-89
[3] M. J. Chmielewski, M. Charon, J. Jurczak, *Org. Lett.* 6 (2004) 20, 3501–3504

P31: Recovery of spent lithium ion batteries for the production of new heterogeneous cobalt catalyst

Giulia Maria Itri [a,b] , **Francesco Mauriello [a]**, **Emilia Paone [a]**

[a] *Università degli studi Mediterranea di Reggio Calabria*
[b] *Università degli studi di Perugia*
giuliaitri@gmail.com

The generation of spent lithium-ion batteries (s-LIBs) worldwide amounts to millions of tons annually. While current recycling methods focus on extracting valuable metals like Ni, Co, and Li, they suffer from poor selectivity, high energy requirements, and expensive by-product management. Consequently, there's growing interest in exploring alternative methods for the direct reuse of s-LIBs [1]. At the same time, lignocellulosic and agro-industrial waste and residues represent a central feedstock for modern biorefineries aimed to the sustainable production of renewable energy and biobased materials and chemicals [2]. Technologies such as hydrothermal carbonization (HTC) have been proposed to upgrade orange peel waste (OPW), yielding hydrochar (OPW-HC) and liquid bio-oil (OPW-OIL), rich in furans derivatives like furfural and 5-HMF, pivotal in modern biorefineries [3]. OPW-OIL can be very rich in furans derivatives (furfural and 5-HMF) that represent one of the most important classes of intermediates in modern biorefineries

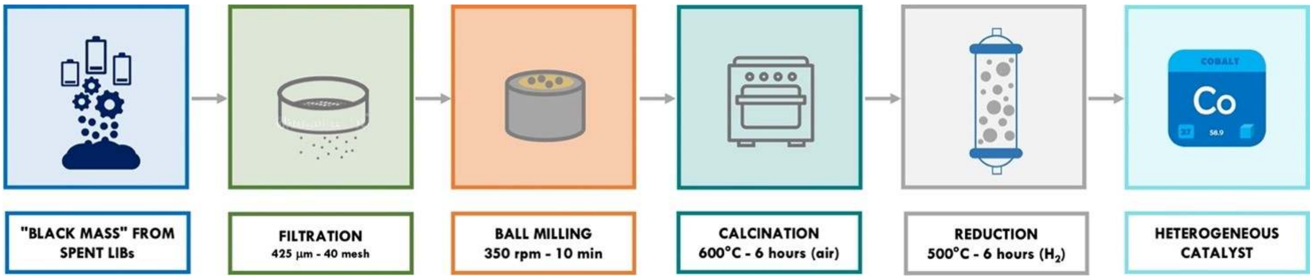


Figure 2 Schematic representation of the mechanothermal treatment of spent LIBs "black mass" for the preparation of Co-based heterogeneous catalysts

Starting from these two abundant wastes, we propose a simple direct approach to transform the s-LIBs into an efficient cobalt-based heterogeneous catalyst. This catalyst has demonstrated excellent efficiency in the upgrading reactions of biomass derivatives

---

[1] E. Paone, M. Miceli, et al., ACS Sustain. Chem. Eng. 2022, 10 (7), 2275-2281.
[2] C. Xu, E. Paone, et al., Chem. Soc. Rev. 2020,49, 4273-4306.
[3] A. Satira, E. Paone, et al., Applied Sciences 2021, 11 (22), 10983

P32: Influence of the activation atmosphere on the catalytic performance of cobalt oxide

<u>Zuzana Kovářová</u>,[1] Tomáš Stryšovský,[1] Martina Kajabová,[1] Libor Kvítek[1]

[1]*Department of Physical Chemistry, Faculty of Science, 17. listopadu 1192/12, 771 46 Olomouc, Palacký University Olomouc, Czech republic*

zuzana.kovarova02@upol.cz

The greenhouse effect and consecutive global warming are the topics most frequently discussed nowadays. Decreasing or even eliminating emissions of CO_2 could be an auspicious way to slow down global warming. This effect can not be stopped, but finding ways to slow it down is possible.[1]

This work is dedicated to hydrogenating CO_2, which could potentially eliminate carbon dioxide emissions and transform them into more valuable products. We use Co_3O_4 as a primary catalyst to achieve the best reduction results.[2]

Activation of the catalyst plays a crucial role in the hydrogenation process. In this work, we study different activation atmospheres under the same conditions. We used three activation atmospheres: He, He+H_2, and reaction atmosphere, which consists of He+H_2+CO_2. Atmospheres were tested for 4 hours at 250 °C. After activation, two reaction temperatures were tested: 250 °C (250_250) and 300 °C (250_300). Both reaction temperatures showed different results (Fig. 1). Which atmosphere could be considered the best for this specific reaction?

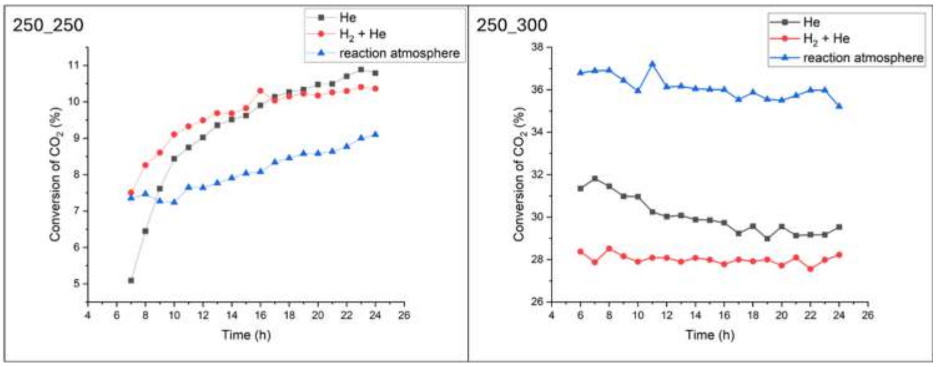


***Figure 1**: Comparison of conversions of CO_2 for three different activating atmospheres under different temperature conditions*

***Acknowledgments**: This work was created with the support of the grant of the Faculty of Science Palacký University in Olomouc, number IGA_PrF_2024_021*

---

[1] P. Sharma et al., *Catal. Sci. Technol.* **2021**, *11*, 1665
[2] M. Wang et al., *Chem. Eng. J.* **2022**, *446*, 137217

P33: LOW VALENT VANADIUM SPECIES IN FERRIERITE ZEOLITE

Mariia Lemishka[1], **Jiri Dedecek**[1], **Kinga Mlekodaj**[1], **Dalibor Kaucky**[1],
Agnieszka Kornas[1], **Edyta Tabor**[1]

[1] J. Heyrovský Institute of Physical Chemistry of the CAS, Dolejškova 3/2155, 182 23 Prague, Czech Republic
mariia.lemishka@jh-inst.cas.cz

Vanadium species incorporated into the zeolite topologies are of significant interest due to their catalytic properties, especially in applications such as selective oxidation, alkylation, and dehydrogenation reactions.[1] Among the factors controlling the catalytic activity, a fundamental role is played not only by the zeolite framework but also by the type of cation, its location, and coordination. Recently, it was shown that in the ferrierite (FER) zeolite transition metal ions, e.g., Fe, Co, Mn, and Ni species, are organized as divalent bare cations located in two adjacent opposite six-membered rings forming the planar β site.[2, 3] This suggests the potential for expanding the group of promising cations that may participate in the formation of binuclear species. The aim of this study was to determine the structure, speciation, and siting of vanadium species in zeolites of the FER matrix for subsequent hydrocarbon oxidation by O_2.

The commercially available Na, K-FER with Si/Al 8.6 was employed as the parent material to obtain V-FERs with varying amounts of vanadium extra-framework species. The initial step involved the ion exchange of the Na, K-FER, yielding the NH_4- and Na-forms of FER. Subsequently, two series of V-FERs were prepared with vanadium loadings ranging from 0.5 to 2.0 wt.%, using two different precursors, VCl_2 (VNH_4-FER) and $VOSO_4*xH_2O$ (VNa-FER) in aqueous solution. The analysis of vanadium species in the FER matrix was conducted using H_2-TPR, in-situ UV-Vis, and FTIR spectroscopy. In-situ FTIR spectra of VNH_4-FER evacuated at 450 °C samples exhibited bands at around 890, 913, and 930 cm^{-1}, which attributed to the antisymmetric T-O-T vibrations of FER rings perturbed by the ligation of bare metal divalent cations.[3,4] This is a typical occurrence for M(II) located in γ, β, and α cationic positions in zeolites, respectively.[4] The FTIR spectra of d_3-acetonitrile adsorbed on dehydrated samples of VNH_4-FER demonstrated the presence of bare V(II) ions, as evidenced by a band at 2305 cm^{-1}, which reflects the presence of Lewis acid sites. Furthermore, the treatment of VNH_4-FERs with O_2 at RT resulted in the disappearance of the bands attributed to V(II) cations, leading to the formation of a new band at around 878 cm^{-1}. This band was proposed as a benchmark for the divalent oxo-cationic species (α-O).[2] Subsequently, methane interacted with the V(IV)=O, resulting in a reduction of vanadium species, and the band characteristic of V(II) in β positions reappeared. In-situ FTIR spectra of dehydrated VNa-FER samples in the T-O-T vibrations region exhibit a single band at 902 cm^{-1}, which may be indicative of the formation of vanadyl species (V=O). The FTIR spectra of d_3-acetonitrile adsorbed on dehydrated samples of VNa-FER didn't confirm the presence of the band at 2305 cm^{-1}, indicating the presence of higher-valent species in the samples. The interaction of VNa-FER with O_2 and CH_4 at RT didn't result in any discernible changes in the FTIR spectrum.

In conclusion, the combination of characterization techniques validated the impact of the preparation method and the selected precursor on the nature and location of the vanadium species in the FER matrix.

Acknowledgments: *This work was supported by the Czech Science Foundation under project # 23-07085X.*

---

[1] K.R. Reddy, A.V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 143, **1993**, 275.
[2] E. Tabor, J. Dedecek, K. Mlekodaj, Z. Sobalik, P.C. Andrikopoulos, S. Sklenak, *Sci. Adv.*, 6, **2020**, eaaz9776
[3] K. Mlekodaj, M. Lemishka, S. Sklenak, J. Dedecek, E. Tabor, *Chem. Commun.,* 57, **2021**, 3472-3475
[4] Z. Sobalik, Z. Tvaruzkova, B. Wichterlova, *J. Phys. Chem.* B, 102, **1998**, 1077-1085

P34: Photoredox Catalysis Enabling Substrate-Dependent Chemodivergent Ritter-Type Carboamidation and Heck-Type Reaction of Olefins

Mattia Lepori,[1] Indrasish Dey,[1] Cassie Pratley,[1] and Joshua P. Barham[1,2]

[1] Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany.
[2] University of Strathclyde, 295 Cathedral Street, Glasgow G11XL, UK.
Mattia.Lepori@chemie.uni-regensburg.de

The Ritter reaction is a well-established method for accessing C–N bonds, generating amides through the reaction of carbocations and nitriles.[1] Since its inception in 1948,[2] the Ritter reaction progressed towards milder and more sustainable conditions, thereby expanding the carbocation precursor pool, especially by means of photoredox catalysis (PRC) and radical polar crossover (RPC).[3] Within this area, tandem radical addition/oxidative RPC emerged as valuable platform for difunctionalization reactions, enabling the incorporation of two distinct, orthogonal functionalities (*e.g.* into C=C double bonds of alkenes) in cascade processes, without the need to isolate intermediates. However, further methodologies are required to tame highly reactive species, such as primary radicals. Herein, we report a three-component carboamidation process harvesting non-stabilized primary radicals (**Figure 1**).[4] In particular, a redox-neutral photocatalytic single electron transfer (SET) approach was leveraged to generate nucleophilic carbon radicals from readily-accessible carboxylic acid-derived redox active esters, the former of which add to aryl olefins as Giese-type acceptors. The resulting benzylic radicals undergo oxidative RPC, generating carbocations that are subsequently trapped by a nitrile in the Ritter-type step, yielding a wide range of difunctionalized products, including late-stage functionalized derivatives of bioactive scaffolds. Furthermore, it was found that Heck-type products were chemoselectively obtained by simply switching aryl olefin acceptors with 1,1-diaryl olefins. In the context of substrate-dependent chemodivergence,[5] various trisubstituted alkenes were synthesized. Utility of our method was demonstrated by efficient scale-up (up to 4 mmol scale) of both decarboxylative processes, in batch and flow.

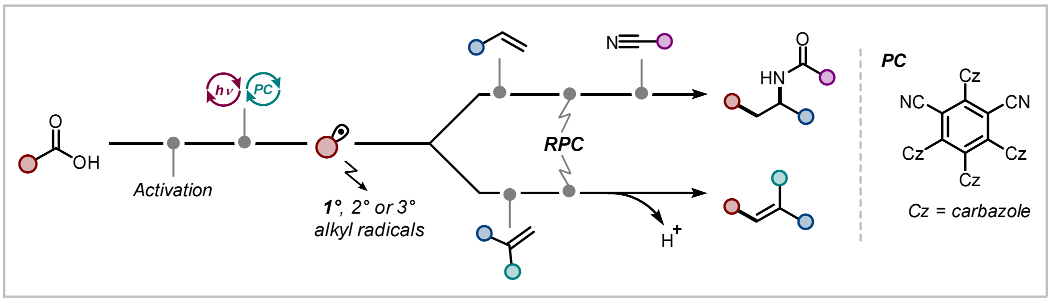


***Figure 1**: Photoredox catalyzed switchable decarboxylative carboamidation and alkenylation.*

---

[1] *i) ChemistrySelect* **2020**, *5*, 14349–14379; *ii) Org. Chem. Front.* **2021**, *8*, 4623–4664.
[2] *i) J. Am. Chem. Soc.* **1948**, *70*, 4045–4048.; *ii) J. Am. Chem. Soc.* **1948**, *70*, 4048–4050.
[3] M. Lepori, I. Dey, C. Pratley, J.P. Barham, *Eur. J. Org. Chem.* **2024**, e202400840.
[4] *Manuscript in preparation.*
[5] Y. Sakakibara, K. Murakami, *ACS Catal.* **2022**, 1857-1878.

P35: Continuous synthesis of limonene oxide using visible light mediated by TitaniaSun

Giovanna Li Petri,[1] **Mario Pagliaro**,[1] **Francesco Parrino**,[2] **Rosaria Ciriminna**[1]

[1]*Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy*
[2]*Dipartimento di Ingegneria Industriale, Università di Trento, via Sommarive 9, 38123 Trento*
giovanna.lipetri@cnr.it

The *trans* isomer of limonene oxide (1,2-limonene epoxide) is the key precursor of poly(limonene carbonate) and poly(limonene) dicarbonate, two biobased polycarbonates showing superior optical, mechanical and thermal properties when compared to conventional polycarbonate derived from bisphenol-A[1]. In 2018, we reported the solar synthesis of LO via photocatalytic oxidation of limonene using O_2 at room temperature and ambient pressure as primary oxidant and TitaniaSun, a silylated version of P-25 titania, as photocatalyst[2]. Recently, the origins of the enhanced selectivity of TitaniaSun compared to P-25 have been correlated with both the higher amount of singlet oxygen in the presence of TitaniaSun and the stabilization of Ti^{3+} centers, whose concentration increases upon silanization[3]. In the original study, we concluded that the yield in LO "may be further improved by integrating the reacting system with a separation unit capable of continuously extracting the desired epoxide from the photocatalytic suspension thus avoiding its overoxidation"[2].

Now we report the preliminary findings concerning the continuous synthesis of limonene oxide using visible light mediated by TitaniaSun. The use of a sol-gel oxide such as TitaniaSun in photocatalytic aerobic oxidation in liquid phase under continuous flow offers several distinctive advantages over reactions in batch[4]. The reaction for instance is faster, more selective and can be carried out without solvent further lowering the E factor of the conversion.

In this presentation, I will report the first results obtained using a commercial continuous flow photoreactor of low-cost and excellent reliability. The process, I will show in the conclusions, holds significant applicative potential for the commercial synthesis of limonene oxide.

Acknowledgements: *Work of G.L.P. was financially supported by the Made in Italy - Circular and Sustainable (MICS) Extended Partnership funded by the European Union NextGenerationEU (PNRR - Missione 4, Componente 2, Investimento 1.3 – D.D. 1551.11-10-2022, PE00000004).*

---

[1] F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro, R. Ciriminna, *ACS Omega* **2018**, *3*, 4884-4890.
[2] R. Ciriminna, F. Parrino, C. De Pasquale, L. Palmisano, M. Pagliaro, *Chem. Commun.* **2018**, *54*, 1008-1011.
[3] F. Parrino, et al., *Angew. Chem. Int. Ed.* **2024**, e202414445.
[4] C. A. Hone, C. O. Kappe, *Top. Curr. Chem.* **2019**, *377*:2.

P36: Porphyrin-embedded porous organic polymer as catalyst precursor in oxidative transformations of bio-renewable substrates.

Emile D. Maggott,[1] **Delia A. Haynes**,[1] **Selwyn F. Mapolie**[1]

[1] *Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa*

emile.maggott@scitec.cnr.it

Fossil fuels like natural gas, coal, and petroleum have long been central to chemical manufacturing, but their environmental impact has sparked major concerns. This has led researchers to focus on renewable resources, especially biomass valorization, which offers a more sustainable approach to chemical production. Biomass, rich in lignocellulose, presents exciting opportunities for generating valuable chemicals. A key component, lignin, is a complex biopolymer made up of phenolic subunits and various aromatic compounds. Although lignin holds significant potential, it remains largely underutilized, highlighting the need for further research to unlock its value in chemical valorization.

Figure 1: Example of a metalloporphyrin-embedded porous organic polymer.

This poster presents the synthesis of a porous organic polymer containing metalloporphyrin units within its polymer structure. Copper was incorporated into the polymer matrix, and the material's potential as a catalyst precursor was evaluated for the oxidation of various lignin model compounds. We also explore the optimization of reaction parameters to improve both activity and selectivity of the copper-embedded polymer as a catalyst. Our results demonstrate successful conversion of various bio-renewable alcohols to their corresponding aldehydes and carboxylic acids. Additionally, the copper-loaded porous polymer showed excellent recyclability, retaining its catalytic activity for up to five consecutive cycles.

---

[1] M. Fache, B. Boutevin and S. Caillol, *ACS Sustain. Chem. Eng.*, 2016, 4, 35–46.
[2] S. Adams, E. K. M. Klobodu and A. Apio, *Renew. Energy*, 2018, 125, 755–767.
[3] T. Imai, T. Yokoyama and Y. Matsumoto, J. *Wood Chem. Technol.*, 2012, 32, 165–174.
[4] A. Modak, J. Mondal and A. Bhaumik, *Appl. Catal. A Gen.*, 2013, 459, 41–51.
[5] A. R. Oveisi, K. Zhang, A. Khorramabadi-Zad, O. K. Farha and J. T. Hupp, *Sci. Rep.*, 2015, 5, 1–8.

P37: Electrochemical reduction of 5-hydroxymethilfurfural to 2,5-bis(hydroxymethil)furan with Cu-electrodeposited foam electrodes

Giovanni Malagoli[1], **Giuseppe Fornasari**[1], **Patricia Benito**[1]

[1] *Industrial Chemistry Department "Toso Montanari", University of Bologna, Italy*
giovanni.malagoli4@unibo.it

The valorization of biomass-based molecules is an important route for the production of sustainable chemicals. The electrocatalytic reduction of 5-hydroxymethylfurfural (HMF) is a promising process to obtain 2,5-bis(hydroxymethyl)furan (BHMF), a diol that can be used to produce polymers, fuel additives and crown ethers.[1] Due to the competitive dimerization and oligomerization of HMF, favoured at high HMF concentrations, and the hydrogen evolution reaction (HER), it is required to develop catalysts that can improve BHMF selectivity and lower the reaction overpotential.[2] Herein, the electroreduction of HMF to BHMF was catalysed by copper foam electrodes with different Cu electroactive surface area (EASA), investigating the effect of potential and HMF concentration on performance.

A commercial copper foam catalyst was used as a benchmark, and an improved catalyst was prepared by copper electrodeposition over the commercial foam using a solution of $CuSO_4$ in H_2SO_4. The electroreduction of HMF was carried out in alkaline pH with a borate buffer (pH = 9.2) in a three-electrode three-compartment cell, with a range of HMF concentrations from 5 to 500 mM. Potentials from -0.51V to -0.71V vs RHE were used. Reactions were stopped at an electric charge for a theoretical 20% HMF conversion.

An increase in the Cu EASA by electrodeposition of Cu on the foam increased the selectivity in BHMF and productivity at all the HMF concentrations (Figure 1). Moreover, the oligomerization (represented as C-loss) is reduced, and even completely hindered until 50 mM, likely related to the increase in the dimer (5,5'-bis(hydroxymethyl)hydrofuroin) formation.

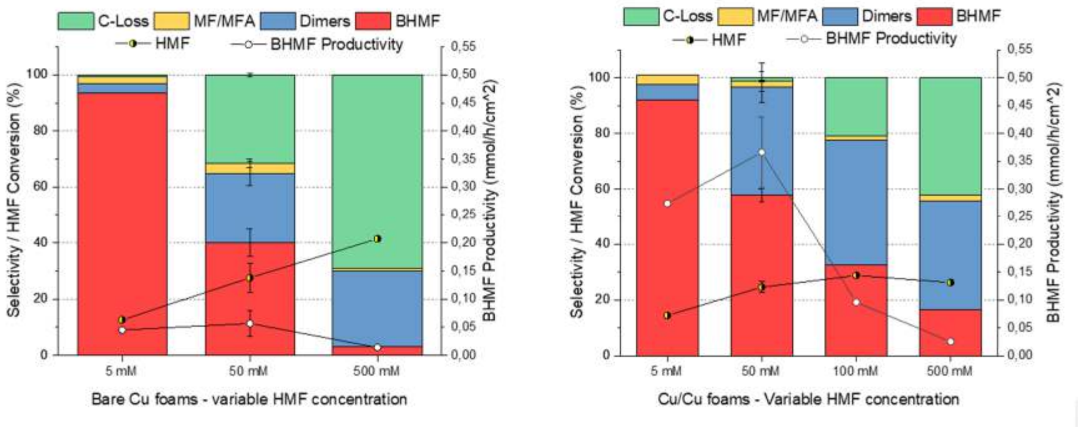


Figure 3. *Catalytic performance of bare vs Cu-electrodeposited Cu-foams at different HMF concentrations.*

---

[1] P. Cornelis et al., *ACS Omega* ***2023***, *8, 10, 8991–9003*

[2] G. S. de Luna et al., *ChemSusChem* **2022**, *15*, e202102504.

P38: Surface Acidity and Basicity of ZnAlGaO$_x$ Catalysts Supports

Laura Milišić,[1] **Blaž Belec,[1] Anja Siher,[1] Gregor Žerjav,[2] Albin Pintar[2], Andraž Mavrič[1]**

[1] *Materials Research Laboratory, University of Nova Gorica, Slovenia*
[2] *Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Slovenia*
laura.milisic@ung.si

Zinc oxide (ZnO) and aluminum oxide (Al_2O_3) are widely used as catalytic supports for CO_2 hydrogenation due to their distinct properties.[1] To influence selectivity, various catalyst supports have been used to modulate the surface properties such as acidity and basicity. For example, basic Ga_2O_3 has been used to partially or fully replace acidic Al_2O_3 to influence adsorption and reaction pathways. Acidic oxides such as Al_2O_3, activate CO_2 by interacting with its electron-deficient carbon atom, facilitating CO_2 conversion. These acidic oxides also play a crucial role in stabilizing methoxy intermediates during the hydrogenation process. Basic oxides ZnO, and Ga_2O_3, on the other hand, adsorbe CO_2 through carbonate formation and stabilize formate intermediates.[2,3]

We present the preparation of ZnAlGaO$_x$ mixed metal oxide catalyst supports derived from the ZnAlGa-layered double hydroxide (LDH) with hydrotalcite structure. Mixed metal LDHs were synthesized via co-precipitation and calcined at 400°C for 3 hours in oxygen to prepare mixed metal oxides. We use powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), along with energy-dispersive X-ray spectroscopy (EDS) to analyze the precursors and catalysis support. The preparation method proved successful in obtaining a uniform distribution of incorporated metal ions.[4] The surface acidity was probed by pyridine temperature-programmed desorption (TPD), and interactions with CO_2 were analyzed by *in situ* DRIFTS CO_2 adsorption/desorption measurements. The findings highlight the potential of mixed metal systems for advancing CO_2 hydrogenation applications.

Acknowledgments: *This work was supported by the Slovenian Research and Innovation Agency (Research Core Funding No. P2-0412 and P2-0150 and Project No. J2-50058.*

---

[1] G.Pacchioni, *ACS Catalysis* **2024**, *14*, 2730-2745.
[2] F. Benaliouche, Y. Boucheffa, P. Ayrault, S. Mignard, P. Magnoux, *Microporous and Mesoporous Materials* **2008**, *111*, 80-88.
[3] Z. Liu, J. Li, Y. Tan, L Guo, Y. Ding, *Catalysts* **2022**, *12*, 1170.
[4] A. Mavrič, G. Žerjav, B. Belec, M. Roškarič, M. Finšgar, A, Pintar, M. Valant, *ChemCatChem* **2024**, *15*, e202300428.

P39: FROM SEWAGE SCUM UP TO LIPIDS PRODUCTION USING OLEAGINOUS YEASTS AS BIOCATALYSTS

Nelly Morrone[1], Nicola Di Fidio[1], Valeria D'Ambrosio[2], Claudia Antonetti[1], Anna Maria Raspolli Galletti[1], Carlo Pastore[2]

[1]Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy
[2]Water Research Institute (IRSA), National Research Council (CNR), Viale De Blasio 5, 70132 Bari, Italy
nelly.morrone@dottorandi.unipg.it

Biodiesel is one of the most promising biofuels in the transportation sector and it is composed of long-chain alkyl esters of fatty acids (FAMEs), which can be obtained from various renewable raw materials, mainly from oilseed crops. Recently, microbial lipids, namely *single-cell oils* (SCOs), have received great interest as feedstocks for biodiesel production due to the advantages given by their use with respect to vegetable oils[1]. Among the oleaginous microorganisms, yeasts are the most promising lipid-accumulating microbes due to their ability to grow fast, independently from environmental conditions and utilize a wide range of carbon sources. Moreover, the economic and ecological feasibility of the yeast lipids production process can be enhanced by using low-cost raw materials[2], such as sewage scum (SS), a special waste obtained from urban wastewater treatment plants. SS is made up of a polysaccharide fraction[3], which can be used as a potential source of fermentable sugars for the bioaccumulation of lipids with oleaginous yeasts after carrying out the hydrolysis reaction. In this context, the aim of this work was the valorization of the hydrolysate obtained through enzymatic hydrolysis of SS toward the production of SCOs, using a biological catalytic approach based on oleaginous yeasts fermentation. *Trichosporon oleaginosus* was used as a biocatalyst for the fermentative process of undetoxified real substrate. In order to optimize the fermentation of sewage scum hydrolysate (SSH) by *T. oleaginosus* in terms of lipid accumulation, three different C/N ratios were investigated (C/N ratios of 80 g/g, 100 g/g and 120 g/g). At the end of the fermentations, standard acidic cell lysis and liquid-to-liquid extraction of SCOs were carried out, and the main outputs of the bioprocesses were calculated, including intracellular lipid content. The results highlighted that *T. oleaginosus* was able to grow on SSH and to consume almost all glucose and xylose. In addition, the C/N ratio of 80 g/g seemed to be a good compromise to facilitate both the biomass growth and the lipids accumulation by *T. oleaginosus.* In detail, adopting this yeast, the SCOs accumulation of 45.6 wt% was achieved. The FAMEs profile of SCOs obtained in this investigation resulted very similar to those of common vegetable oils, used at the industrial scale for commercial applications, including the production of traditional biodiesel.

Acknowledgments: *The authors thank the PRIN 2022-Project ReFil "Renewable liquid Fuel of new generation from wastewater sludge: a step towards circular economy" (code 2022KA5WL8).*

---

[1] I. C. Kuan *et al.*, *Energies*, **2018**, 11, 1036-1044
[2] P. Shaigani *et al.*, *Microbial Cell Factories*, **2020**, 20, 220-237
[3] L. di Bitonto *et al.*, *Renewable Energy*, **2016**, 90, 55-61

P40: Impact of the synthesis protocol on the electrocatalytic activity of NiO towards nitrate reduction to ammonia

<u>Andrea Muscatello</u>[1], Alessandro Padua[1], Lorenzo Sibella[1], Sara Garcia Ballesteros[1], Serena Esposito[1], Federico Bella[1]

[1] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129 - Torino, Italy*
andrea.muscatello@polito.it

Ammonia is a versatile chemical compound with numerous applications. Overcoming the limitations of the Haber-Bosch process is a crucial frontier for innovation, to produce NH_3 through environmentally friendly and sustainable processes. An excellent candidate is the electrochemical nitrogen reduction reaction (E-NRR), which can be powered by electricity from renewable sources such as solar and wind energy and proceed under ambient conditions. Recently, attention has shifted toward NO_3^- reduction, offering the potential to purify waters with high NO_3^- content caused by the widespread use of nitrate-containing fertilizers in agriculture.

Nickel oxide (NiO) could be an excellent candidate as a catalyst because nickel is a low-cost, robust transition metal, and possesses outstanding electrochemical properties. Indeed, NiO-based systems, particularly those supported on other oxides or porous materials, have been a focal point of recent research, alongside metallic Ni-based catalysts [1]. To strengthen these experimental findings, density functional theory calculations have demonstrated that nickel exhibits excellent activity in electrochemical ammonia production [1]. Based on the previous consideration, we have investigated the effect of different preparation methods on the physicochemical properties of unsupported NiO, as well as its performance in ammonia production from NO_3^- ions, and its Faradaic efficiency. Moreover, since the literature lacks extensive reports on the influence of NiO morphology on NH_3 productivity, we investigated the effect of NiO morphology on the electrocatalytic hydrogenation of N_2 or NO_3^-. In detail, we have explored hydrothermal synthesis and precipitation in aqueous and hydroalcoholic media to obtain NiO samples with diverse microstructures, followed by thermal treatment under varying conditions. X-rays diffraction (XRD) was used to characterize the structures and to assess the phase purity. The textural properties were obtained through N_2 adsorption/desorption isotherms. Scanning electron microscopy (SEM) was used to examine the resulting morphologies. Finally, electrocatalytic reduction tests of nitrogen and nitrates were performed in an H-type cell to assess the catalyst Faradaic efficiency and production rate.

Acknowledgements: *This project received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No. 948769, project title: SuN$_2$rise).*

---

[1] L. Ouyang, J. Liang, Y. Luo, D. Zheng, S. Sun, Q. Liu, M. S. Hamdy, X. Sun, B. Ying, *Chinese j. catal.* **2023**, 50, 6-44.

P41: ETHANOL TO GASOLINE AND SUSTAINABLE AVIATION FUEL PRECURSORS: AN INNOVATIVE CASCADE STRATEGY OVER ZR-BASED MULTIFUNCTIONAL CATALYSTS IN THE GAS PHASE

Maria Pagliara,[1] **Anna Gagliardi**,[1] **Giulia Balestra**,[1] **Jacopo De Maron**,[1] **Rita Mazzoni**,[1] **Fabrizio Cavani**[1], **Tommaso Tabanelli**[1]

[1] *Dipartimento di Chimica Industriale "Toso Montanari", viale Risorgimento, 4, Bologna 40136, Italy*
maria.pagliara2@unibo.it

The production of alternative fuels from biomass is a topic of enormous interest for both academic and industrial research, due to the urgency to break free from fossil resources and achieve a more sustainable circular economy. The aviation industry is in the spotlight because of its dependence on fossil resources for jet fuel, the generic name for aviation fuels used in gas turbine-powered aircraft. Greenhouse gas (GHG) emissions from international aviation have increased by about 130% over the past two decades, the largest increase in the entire transport sector. Industry associations, governments and airlines are investing considerable resources in alternative fuels, generally classified as sustainable aviation fuels (SAFs). SAFs are produced using renewable energy, biomass or waste resources.[1] They offer the same performance as petroleum-based aviation fuel, but with a fraction of its carbon footprint, thus reducing GHG emissions from flying. Various alcohols currently derived from renewable raw materials have been considered for SAF production, among which the greatest interest is in ethanol processes, since bioethanol is the most widely used renewable energy source in the world. Herein, the gas-phase, continuous flow catalytic upgrading of ethanol to blends with features close to those suitable for jet fuel is tackled through an innovative strategy based on the promotion of several reactions in cascade. Catalytic transfer hydrogenation, aldol condensation, dehydrogenative coupling, and ketonization reactions were combined in a one-pot approach over a relatively simple and cheap catalytic system consisting of copper nanoparticles supported on zirconium (and lanthanum) oxides. The resulting cascade reaction scheme led to the production of a blend of compounds in the C6-C14 range, including linear and branched esters, linear and branched alcohols, linear, branched and cyclic ketones, aldehydes, alkenes and aromatics (hydrocarbons and phenolics), which showed similar properties to those of Jet A and A-1 fuels, the most widespread worldwide. By tailoring the features of the non-innocent support and/ or co-feeding hydrogen to the reactor, up to 40% selectivity for the jet fuel range fraction, with ethanol conversion above 85%, was achieved during the first 6 h of time on stream, simultaneously enhancing catalyst stability and lifetime.[2] Even though more work is needed to optimize the catalytic material, increasing its lifetime and fostering acetaldehyde conversion, the obtained blends could be potentially used as jet fuel or jet fuel additive after a few preliminary operations such as the distillation of the lighter compounds and a mild hydrogenation process in order to stabilize aldehydes and unsaturated compounds.

---

[1] R. Mawhood, E. Gazis, R. Hoefnagels, S.D. Jong, Technological and commercial maturity of aviation biofuels: Emerging options to produce jet from lignocellulosic biomass, (**2015**) 10.

[2] Gagliardi, A.; Balestra, G.; De Maron, J.; Mazzoni, R.; Tabanelli, T.; Cavani, F. Ethanol to Gasoline and Sustainable Aviation Fuel Precursors: An Innovative Cascade Strategy over Zr-Based Multifunctional Catalysts in the Gas Phase. Applied Catalysis B: Environment and Energy **2024**, 349, 123865. https://doi.org/10.1016/j.apcatb.2024.123865.

P42: Heterogenous Cu Single Atom- based C-S coupling reactions for the synthesis of pharmaceuticals

Shilpa Palit,[1] **Theodore A. Gazis**,[1] **Gianvito Vilè**[1,*]

[1] *Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)*
shilpa.palit@mail.polimi.it

Carbon-heteroatom cross-coupling reactions are foundational in organic chemistry, providing efficient access to a wide range of pharmaceuticals, agrochemicals, and organic electronics. Among the most important motifs in these reactions are C–O, C–N, and C–S bonds, with organosulfur functionalities being of particular significance. For example, over 300 FDA-approved drugs exhibit a wide spectrum of biological activities, many of which contain a C–S bond in their structure.[1] Despite their importance, the development and understanding of catalytic C–S couplings have lagged behind C–N and C–O couplings due to two main challenges: (a) C–S bonds are prone to oxidation, forming disulfides during synthesis, and (b) sulfur's high affinity for transition metals can lead to catalyst poisoning and rapid catalyst deactivation.[2] As a result, the development of heterogeneous catalysts for selective and efficient C–S coupling reactions remains in its early stages. Given the prevalence of organosulfur compounds in industrial targets, developing recyclable and robust catalysts for their synthesis is of critical importance to align industry with the UN sustainable development goals. The integration of Single Atom Catalysts (SACs), which exhibit 100% atom utilization and exceptional stability, presents an elegant solution to these challenges. To this end, we utilized a modified literature approach to anchor Cu single atoms on mesoporous graphitic carbon nitride (mpgCNx) catalysts (Cu-mpgCNx). A battery of characterization techniques (ICP, XRD, XPS, TEM, XAS, BET, IR, NMR) were employed to confirm the uniform dispersion and single-atom nature of the catalyst. With a detailed understanding of the Cu-mpgCNx catalyst, we employed it for the first time in the coupling reaction of thiols with aryl halides. Our developed protocol displayed broad tolerance toward various functional groups, including heterocycles and sterically demanding substrates. In addition, we achieved the synthesis of important pharmaceuticals, such as the mycolytic agent carbocisteine and the antidepressant vortioxetine, as well as targeting the late-stage derivatization of captopril and iodopamidol.

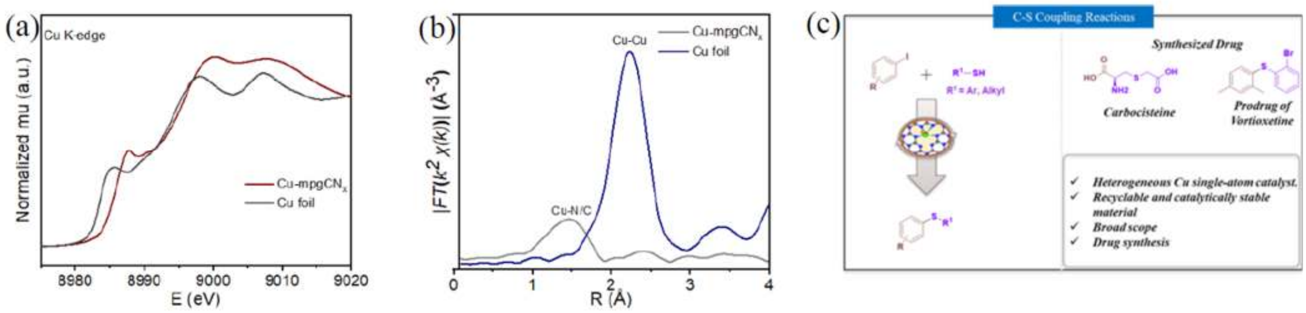


Figure 1: *Normalised magnitudes of (a) X-ray absorption near edge spectra (b) k2- weighted Fourier transform (FT) of the extended X-ray absorption fine structure spectra in radial distance (R), (c) schematic representation of C-S coupling reaction with the heterogenous catalyst.*

References:

[1] M. Feng, B. Tang, S.H. Liang, X. Jiang, *Curr.Top.Med.Chem.* **2016**, 16, 1200-1216.
[2] J. Louie, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, 117, 11598– 11599.

P43: BASE METAL NANOPARTICLES STABILIZED IN ALTERNATIVE REACTION MEDIA FOR CROSS-COUPLING REACTIONS

Eleonora Palmerini,[1] **Mustapha Hamdaoui**[1], **Katalin Barta**[1]

[1] *Institute of chemistry, University of Graz, Austria*
eleonora.palmerini@uni-graz.at

Cross-coupling has become one of the most common catalytic processes used for the generation of pharmaceutical candidates. However, since cross coupling was invented in the 1970s, it has always been conducted with precious metals, mostly Pd, which suffer from sustainability and economic issues and will face supply limitations in the future.[1] However, a very promising approach would be to catalyze cross-coupling reactions by using active *metal nanoparticles (NPs)* generated and stabilized in *ionic liquids* (ILs) with a focus on abundant metals such us Mn, Fe, Co, Ni, Cu, which are usually less costly and less toxic.[2] Moreover, by nature, *in situ* generated metal NPs in alternative reaction media offer process simplicity and the possibility for catalyst recycling, which also presents an important issue in terms of methodology development and overall process sustainability. Furthermore, given the importance of the synthesis of aromatic amines in the manufacturing of many pharmaceuticals, Buchwald-Hartwig amination was chosen as the reaction of choice for our study. Commonly, this type of reaction requires a palladium precursor in combination with carefully designed ligands as catalyst, a base, as well as amines and aryl-halides or pseudohalides (*e.g.* aryl tosylates) as substrates.[1] In this work, we have set out to investigate a new approach to catalytic amination of aryl halides by non-noble metal NPs in IL media. To the best of our knowledge, only very limited examples of non-noble metal nanoparticles in ILs for C–N cross couplings are reported, probably due to the minor reactivity/versatility of these metals and the struggle of these catalytic systems to survive in such basic environments. [3-4] While such NP systems have been extensively investigated for (de)hydrogenation reactions, less attention was devoted to investigating their catalytic activity in cross coupling reactions. Hence, we believe that this is a very promising research area of study with much unrealized potential.

---

[1] Hartwig, John F. *Organotransition Metal Chemistry: From Bonding to Catalysis.* **2010**, Sausalito (Calif.): University Science Books.
[2] Dupont, J.; Leal, B. C.; Lozano, P.; Monteiro, A. L.; Migowski, P.; Scholten, J. D. *Chem. Rev.* **2024**, *124* (9), 5227–5420.
[3] Keßler, M. T.; Robke, S.; Sahler, S.; Prechtl, M. H. G. *Catal. Sci. Technol.* **2014**, *4* (1), 102–108.
[4] Geukens, I.; Fransaer, J.; DeVos, D. E. *ChemCatChem* **2011**, *3* (9), 1431–1434.

P44: Supramolecular asymmetric organocatalysis via miminalistic peptides

Martina Porco,[1] **Alessio Carioscia,[1] Fabio Pesciaioli,[1] Armando Carlone[1,2]**

[1] Department of Physical and Chemical Sciences, Università degli Studi dell'Aquila, via Vetoio, L'Aquila, Italy
[2] INSTM, Consorzio Nazionale per la Scienza e Tecnologia dei Materiali, RU L'Aquila, Italy
martina.porco@student.univaq.it

It is well known that organocatalysis has brought significant advantages to asymmetric catalysis complementing enzymatic and transition metal catalysis. This is due to the use of cost-effective organocatalysts that are often available in enantiopure form and are easy to handle.[1] However, organocatalysis sometimes bears some limitations such as low catalytic efficiency, or low turnover number (TON) and turnover frequency (TOF). One promising strategy to overcome these drawbacks is the use of supramolecular catalysts, which can self-assemble into organized structures through electrostatic interactions triggered by external stimuli, such as changes in solvent or pH.[2]

Peptides have been studied as supramolecular organocatalysts, aiming to emulate enzymatic catalysis with the use of low molecular weight molecules. Proline derivatives are often used as a building block in these systems due to their well-known ability as an organocatalyst.[3]

It was recently demonstrated that the tripeptide ^{D}PFF is able to self-assemble into fibrils under specific conditions in aqueous solution.[4] Building on this observation, we decided to explore the use of fibrils as supramolecular organocatalysts, showing that ^{D}PFF fibrils can increase the conversion rate in Michael addition reactions compared to non-self-assembled ^{D}PFF.[5] The acceleration on catalysis imparted by fibrils is probably due to the formation of hydrophobic pockets where reactants are concentrated, bringing them closer to each other and the catalytic proline site. Furthermore, the use of water as a solvent makes the reaction more eco-friendly and sustainable, aligning with the principles of green chemistry.

In light of the obtained results, we aim to explore different peptide sequences to evaluate their ability to form supramolecular structures and explore various substrate activation mechanisms, including enamine and iminium pathways, H-bond and NHC activation, the last one using a terminal histidine residue.

---

[1] D. W. C. MacMillan, *Nature* **2008**, *455*, 304–308.

[2] F. Pesciaioli, V. Nori, A. Sinibaldi, A. Carlone, *Asymmetric Organocatalysis* **2023**, John Wiley & Sons, Ltd, 271–317.

[3] P. Melchiorre, M. Marigo, A. Carlone, G. Bartoli, *Angew. Chem. Int. Ed Engl.* **2008**, *47*, 6138–6171.

[4] A. M. Garcia, M. Melchionna, O. Bellotto, S. Kralj, S. Semeraro, E. Parisi, D. Iglesias, P. D'Andrea, R. De Zorzi, A. V. Vargiu, S. Marchesan, *ACS Nano* **2021**, *15*, 3015–3025.

[5] A. Sinibaldi, F. Della Penna, M. Ponzetti, F. Fini, S. Marchesan, A. Baschieri, F. Pesciaioli, A. Carlone, *Eur. J. Org. Chem.* **2021**, 5403–5406.

P45: A unified approach for the synthesis of 5-membered heteroaromatics by combining decatungstate photocatalysis and Paal-Knorr reaction in flow

Luna Raineri,[1] **Filippo Sacchelli**,[1] **Marzia Pessina**,[1] **Nicola Della Ca'**,[1] **Luca Capaldo**[1]

[1] *SynCat Lab, Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy.*
luna.raineri@unipr.it

Heteroaromatic compounds are highly sought after in pharmaceuticals, agrochemicals, and materials science, making the rapid synthesis of these molecules crucial. A key approach to accessing these valuable motifs is the Paal-Knorr method, particularly for synthesizing five-membered heterocyclic compounds such as furans, thiophenes, pyrroles. This method relies on the availability of 1,4-diketones. As a result, considerable efforts have been made to develop efficient strategies for preparing such compounds[1,2]. One particularly convenient approach is the tetrabutylammonium decatungstate (TBADT)-photocatalyzed hydrogen atom transfer (HAT) acylation of electrophilic olefins, which starts from readily available starting materials like aldehydes and α,β-unsaturated carbonyl compounds[3].

In this study, we present a unified strategy for a streamlined two-step synthesis of heteroaromatics, combining decatungstate photocatalysis and the Paal-Knorr reaction under flow conditions (Figure 1). The first step is a photocatalytic one that involves the reaction between an aldehyde and a vinyl ketone to form a 1,4-diketone via TBADT photocatalyzed HAT reaction. The second step is a cyclization one using amines, Brønsted acids, Lawesson's reagent to yield pyrroles, furans, thiophenes, respectively.

This approach stands as a straightforward and scalable route to these commercially important scaffolds.

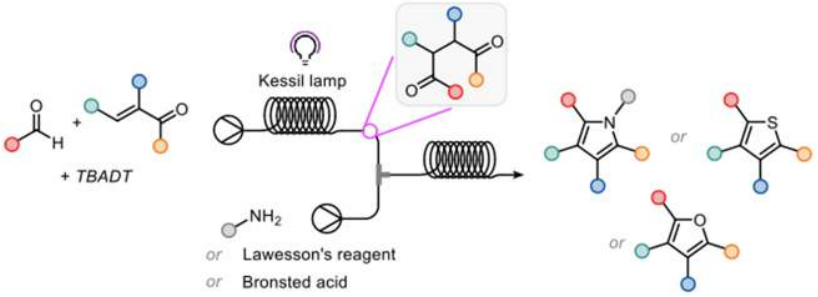


Figure 1*: A unified telescoped approach for the synthesis of 5-membered heteroaromatics.*

---

[1] M. Lemmerer, M. Schupp, D. Kaiser, N. Maulide, *Nat. Synth*, **2022**, *1*, 923–935.

[2] A. Balakrishna, A. Aguiar, P. J. M. Sobral, A. J. F. N. Sobral, *Catal Revs*, **2019**, *61*, 84-110.

[3] S. Esposti, D. Dondi, M. Fagnoni, A. Albini, *Angew. Chem. Int. Ed.* **2007**, *46*, 2531–2534.

P46: Study and Development of bifunctional catalysts for the conversion of CO_2 into light olefins

<u>Daniel Rustichelli</u>,[1,2] Alessia Marino,[1,2] Mattia Melloni,[3] Andrea Lazzarini,[1,2] Angelo Ferrando,[3] Marcello Crucianelli,[1,2] Nicola Vecchini,[3] Alfredo Aloise[1,2]

[1] University of L'Aquila, Department of Physical and Chemical Sciences (DSFC), via Vetoio, I-67100 L'Aquila
[2] Consorzio INSTM, via G. Giusti, 9, I-50121 Firenze
[3] Versalis S.p.A., Basic Chemicals & Plastic Research Center, via G. Taliercio, I-46100 Mantova
daniel.rustichelli@student.univaq.it

Converting CO_2 into valuable chemical products represents a key challenge to addressing environmental issues related to climate change. Fossil fuels reserves are running out, prompting research into renewable carbon sources as a sustainable resource. This research project focuses on developing bifunctional heterogeneous catalysts[1], such as functionalized zeolites and composite structures, to convert CO_2 into light olefins[2,3] (Figure 1). Olefins are a key building block for the chemical industry, particularly for the production of polymers, rubbers, and fuels, as well as being the raw material for the synthesis of vinyl acetate monomer (VAM). Currently, its synthesis involves high-risk and unsustainable processes.

This research aims to create new catalytic pathways for both, CO_2 activation and C-C bonds formation, contributing to a deeper understanding of the conversion processes of CO_2 into light olefins and enabling the application of this knowledge to different catalytic systems, thus opening new opportunities for the sustainable utilization of this vital resource. Combinations of zeolites, metals (or oxides) and affordable synthetic methods, will be studied to optimize conversion and selectivity, analyzing parameters such as temperature, pressure, reaction time, and space velocity.

Laboratory tests and catalytic trials in fixed-bed reactors will assess industrial scalability and by-product reduction, employing appropriate analytical characterization techniques (XRD, SEM, TGA, FT-IR, ICP, GC-MS, NMR).

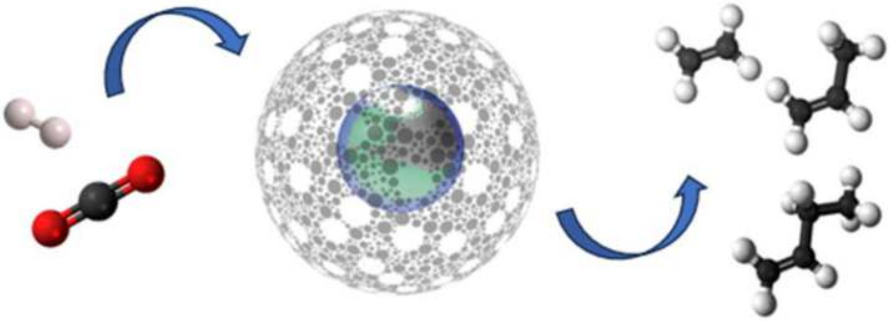


Figure 1: *bifunctional catalyst transforming CO_2 into light olefins (Black = Carbon; White = Hydrogen; Red = Oxygen)*

---

[1] Zhang, Qiao, et al., *Accounts of Chemical Research* **2013**, *46(8)*: 1816-1824.

[2] Marlin, Dana S., Emeric Sarron, and Ómar Sigurbjörnsson, *Frontiers in Chemistry* **2018**, *6*: 446.

[3] Yang, Miao, et al., *Advanced materials* **2019**, *31(50)*: 1902181.

P47: Investigating the mechanism of reductive catalytic fractionation with alternative magnetic catalysts: a model molecule approach

Giuseppe Salierno[1,2], Federico Bugli[1], Marcelo Eduardo Domine[3], Alberto Fernández-Arroyo Naranjo[3], Giovanni Di Liberto[4] Fabrizio Cavani[1,], Tommaso Tabanelli[,1]

[1] *University of Bologna, "Toso Montanari" Department of Industrial Chemistry, Bologna, Italy.*
[2] *University of Perugia, Department of Chemistry, Biology and Biotechnology, Perugia, Italy.*
[3] *Instituto de Tecnología Química (UPV – CSIC), Universitat Politècnica de Valéncia, Valencia, Spain.* [4] *Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Milano, Italy*

giuseppe.salierno@studio.unibo.it

The sustainable valorization of lignocellulosic biomass (LCB) remains challenging for the chemical industry. Lignin-first biorefineries offer a promising approach to valorize all LCB components, particularly lignin, by targeting β-O-4 ether linkages for efficient depolymerization into bio-based aromatic monomers while minimizing parasite recondensations.[1,2] Recent work on $RuOx/\gamma\text{-}Fe_2O_3$ in reductive catalytic fractionation (RCF) of poplar sawdust demonstrated its magnetic separability and excellent recovery and recyclability.[3] Using model molecules to mimic lignin's structural features enables controlled studies of catalytic mechanisms, efficiency, and reaction optimization. Herein, $RuOx/\gamma\text{-}Fe_2O_3$ was compared to the benchmark Ru/C for lignin depolymerization and stabilization under reductive conditions.

Eugenol, vanillin, and a β-O-4 dimer, 2-phenoxy-1-phenylethanol (2P1P), were tested to assess suppression of recondensation and ether bond cleavage respectively. Ru/Fe_3O_4, the active phase formed during the reaction, selectively cleaved β-O-4 bonds while preserving aromaticity, unlike Ru/C, which promoted over-hydrogenation, consuming more H_2 and forming saturated dimers. Interestingly, the magnetic catalyst exhibited larger metal nanoparticles (NPs) compared to Ru/C, which showed better metal dispersion. The results challenge common literature linking smaller metal NPs and better dispersion with orthogonal adsorption and the preservation of aromaticity.[4] The oxyphilic nature of Ru/Fe_3O_4 may promote orthogonal adsorption via hydroxyl groups, generating intermediates that facilitate ether bond cleavage.

Further tests with eugenol and vanillin confirmed Ru/Fe_3O_4 higher selectivity in stabilized products suppressing the over-reduction unlike Ru/C. These findings emphasize the critical role of catalyst support in directing adsorption and reaction pathways, with Pd and Ru on magnetic iron oxides showing promise for selective lignin valorization.

---

[1] E. Paone, T. Tabanelli, F. Mauriello. *Curr. Opin. Green Sustain. Chem.,* **2020**, *24*, 1-6

[2] V. K. Garlapati, A. K. Chandel, S. P. J. Kumar, S. Sharma, S. Sevda, A. P. Ingle, D. Pant, *Renew. Sustain. Energy Rev.* **2020**, *130*, 109977

[3] F. Bugli, A. Baldelli, S. Thomas, M. Sgarzi, M. Gigli, C. Crestini, F. Cavani, T. Tabanelli, *ACS Sus. Chem. Eng.* **2024**, *12, 45*, 16638–16651.

[4] J. Marlowe, P. C. Ford, M. M. Abu-Omar, P. Christopher, *Catal. Sci. Technol.* **2023**, *13*, 5662

P48: Optimization of chemical activation conditions of activated carbons for reversible hydrogen storage

S. Sciarretta, **A. Marino, A. Lazzarini, M. Crucianelli**

DSFC, University of L'Aquila, via Vetoio ("A.C. De Meis" building), 67100 L'Aquila, Italy

The current global economy is desperately hungry for energy and even in the case of increased energy production from non-renewable raw materials (primarily fossil and nuclear), the environmental costs will be enormous. Therefore, it is important to develop efficient technologies and materials to convert electrical energy into chemical energy, usable as needed.

One of the most promising molecules for this purpose is hydrogen. This molecule has enormous potential both as a traditional energy carrier (usable with already established technologies) and as a molecule of high industrial value. One of the major limitations to its widespread use lies in the current technologies for its storage and transport. Due to its low energy density, it needs to be concentrated. However, this storage method can be extremely dangerous.

Therefore, the development of materials for the rapid release of hydrogen (physisorption) is of great practical interest. In this scenario, activated carbons play a leading role being characterized by a high surface area and obtainable from recovered raw materials [1]. The aim of this project is to subject samples of different nature (*i.e.* recovered from biomass and/or industrial sources) and origin to chemical acid and basic activation in order to observe, if present, the influence of the different matrices on the rise of the morphology, for each sample.

Figure: *Schematic representation of the work*

---

[1] S. Li et al. / Microporous and Mesoporous Materials 243 (2017) 291-300

P49: CO-INDUCED PHENOMENA ON SUPPORTED METAL NANOPARTICLES

Elena Seminerio[1,2,3]

[1] *University of Perugia, Italy*
[2] *University of Torino, Italy*
[3] *INSTM, Italy*
elenaseminerio@gmail.com

Precious metal-based catalysts, including Pd, Pt, and Ru, are commonly used in petrochemical, pharmaceutical, and fine chemical industries,[1] typically supported on activated carbons and metal oxides to enhance their activity and stability. CO is commonly used as a probe molecule to study these catalysts, offering insights into the surface properties of metal nanoparticles (NPs), in particular providing the metal dispersion, which is defined as the ratio between the surface and the total atoms in the particle. However, recent studies using gas volumetry, adsorption microcalorimetry, and IR spectroscopy have demonstrated that CO can induce surface roughening in Pd NPs on Al_2O_3.[2] This is particularly relevant in catalysis, because surface and structural changes in the presence of adsorbates can influence the catalytic performance of these materials.[3] In order to achieve a deeper understanding of adsorbate-induced phenomena, we started a systematic investigation on a series of catalysts based on supported metal NPs utilizing the three previously mentioned techniques with CO pulses.

At first, we investigated the influence of the support on Pd-based catalysts, comparing the results of Pd/Al_2O_3 with those obtained for Pd/Cw (being Cw a wood-derived carbon). Volumetric measurements show a standard Type I isotherm for Pd/Cw (opposite to a stepped isotherm for Pd/Al_2O_3), indicating that no CO-induced surface reconstruction takes place in the former, likely due to the larger, irregular size of the NPs and their lack of well-defined crystalline surfaces.

Then we examined the influence of the metal by comparing Pt/Al_2O_3 and Ru/Al_2O_3. For both samples, above a certain P_{CO} threshold, some phenomena involving the metal NPs occur that makes subsequent CO adsorption events more favourable than the previous ones. This behaviour can be deduced from the volumetric measurements, where in the isotherms at least one anomalous step is detected, as well as from the calorimetric measurements, which reveal an increase in the heat of adsorption as CO coverage increases. Furthermore, IR spectroscopy indicates that as CO coverage increases, a turning point is reached, at which a shift in the bands is observed. At this point, the intensity of some bands increases, while that of others decreases. The pressure at the turning point coincides with the one at which the unexpected behaviour is observed in both the volumetric and microcalorimetric measurements.

Overall, CO adsorption induces surface modifications in all investigated systems, regardless of the metal or support; however, further studies are needed to identify the specific surface modifications induced by CO.

---

[1] Z. Luo, G. Zhao, H. Pan, W. Sun, *Adv. Energy Mater.*, **2022**, *12*
[2] A. Ricchebuono et al., *ACS Catal.*, **2024**, *14*, 13736–13746
[3] M. Ahmadi, H. Mistry, and B. Roldan Cuenya, *J. Phys. Chem. Lett.*, **2016**, *7*, 3519-3533

P50: H_2 generation linked to selective oxidation of biomass precursors

Shreya Sharma,[1] **Kylie A. Vincent**[1]

[1] *Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, S. Parks Rd., Oxford, UK*
shreya.sharma@some.ox.ac.uk

Molecular H_2 is a widely used reductant in the chemical industry. With the growing demand in industrially relevant chemical reactions, finding closed-loop, sustainable systems for H_2 production and recycling is critical to reduce the atmospheric implications. The reliance of oxidoreductases on costly cofactors (NAD^+/NADH, $NADP^+$/NADPH) limits their industrial use. The aim of the work is to illustrate suitability of a NAD+ regeneration system based on H_2 evolution. We use NiFe hydrogenase (hydrogenase-2), that operates reversibly E'($2H^+$ /H_2), coupled with NAD reductase in an enzymatic cascade to assemble a catalytic system directed towards sustainable synthesis and valorization of biomass feedstocks[1] (Fig. 1). Conventional NAD+ regeneration systems face many challenges including the use of additional oxidants or production of co-products[2]. These chemically and architecturally integrated nature-based catalysts facilitate electron transfer to carry out chemical reactions in a cost effective and carbon neutral manner while producing H_2 as the only byproduct[3].

The work highlights how potentially in a future sustainable hydrogen economy, biocatalytic hydrogenation could become a core process for clean chemical manufacturing, offering promising ways to store and use energy during peak periods of production. This offers a practically viable, close-loop recycle pathway where the H_2 produced as a byproduct of a biochemical reaction is reused for additional chemical reaction systems minimizing atmospheric emissions and enhancing sustainability, creating a cycle where hydrogen's utility is maximized without adding to environmental impact.

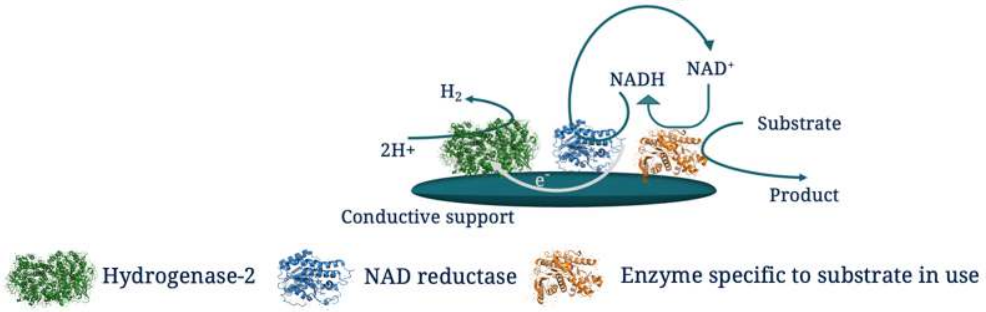


Figure 1: *The hydrogenase based catalytic system for clean chemical synthesis producing H_2 as the only by-product.*

---

[1] Lauterbach, Lars, Oliver Lenz, and Kylie A. Vincent. "H_2-driven cofactor regeneration with NAD (P)+-reducing hydrogenases." *The FEBS journal* 280.13 (2013): 3058-3068.

[2] Al-Shameri, Ammar, et al. "Hydrogenase-based oxidative biocatalysis without oxygen." *Nature Communications* 14.1 (2023): 2693.

[3] D. Sokolava, K.A. Vincent, "Exploiting hydrogenases for biocatalytic hydrogenations," Chem. Commun. (2024), DOI: 10.1039/D4CC04525D

P51: 2,6-DIIMINOPYRIDINE-BASED ORGANOMETALLIC PRE-CATALYSTS: SYNTHETIC STUDIES AND CATALYTIC APPLICATIONS

Simone Stampatori,[1] Nassima Yamini,[1] Valeria Iacomini,[1,2] Alessio Nicolini,[1] Manuel Imperato,[1] Andrea Cornia,[1] Francesca Parenti,[1] Giuliano Fiscaletti,[3] Angelo Ferrando[4]

[1]*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy*
[2]*Department of Physics, Informatics and Mathematics, University of Modena and Reggio Emilia, Modena, Italy*
[3]*Research center Ravenna, Versalis S.p.A, Ravenna, Italy*
[4]*Research center Mantova, Versalis S.p.A, Mantova, Italy*
simone.stampatori@unimore.it

In modern catalysis, a major challenge concerns the employment of precious metals in homogeneous processes. Although rare metal-based catalysts are essential for the production of fine chemicals and other commodities, obstacles like unstable market prices, a shortage of supply, toxicity, and environmental effects have prompted researchers to look at first-row transition metals as sustainable substitutes.[1]

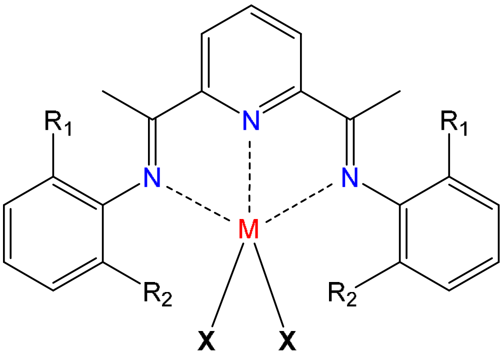


Figure 1. Structure of ^{R_1,R_2}PDI metal complexes

Specifically, in olefin chemistry first-row transition metal complexes with 2,6-diiminopyridines (^{R_1,R_2}PDI) and X = alkyl (*Fig. 1*) have demonstrated to be outstandingly efficient pre-catalysts.[2] However, they are highly air-sensitive and thermally unstable, making their storage, transport, and large-scale production demanding.

Herein we propose an *in-situ* assembly protocol to generate [(^{R_1,R_2}PDI)MX_2] compounds, involving a relatively stable organometallic precursor [(L)MX_2], the appropriate ^{R_1,R_2}PDI ligand, and an auxiliary inorganic lithium salt to promote the removal of the labile ligand L. This ligand exchange reaction takes place in an organic solvent with promising conversions, as established *via* ^{1}H NMR spectroscopy. Furthermore, the conversion rises as the steric hindrance of the R_1 and R_2 substituents of the aryl groups decreases.

This *in-situ* preparation was employed in a benchmark hydrosilylation reaction between 1-octene and triethoxysilane. Conversion and selectivity, evaluated *via* ^{1}H NMR spectroscopy and GC-MS analyses, range from good to excellent and are comparable with those provided by the same pre-catalysts prepared *ex-situ*.[2]

Hence, our method supplies a feasible strategy for the assembly of ready-to-use [(^{R_1,R_2}PDI)MX_2] pre-catalysts in organic solution and encourages their application in industrial-grade organic reactions.

---

[1] Supanchaiyamat, N.; Hunt, A. J.; *ChemSusChem* **2019**, *12*, 397–403
[2] Obligacion, J. V.; Chirik, P. J; *Nat. Rev. Chem.* **2018**, *2*, 15–34

P52: Light-Driven Aerobic Cleavage of Unsaturated Fatty Acids into Industrially Relevant Carbonyl Compounds

Sara Stocchetti,[1,2] Alberto Luridiana,[1] Francesco Secci[1]

[1] *Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Italy.*
[2] *Dottorato di Interesse Nazionale in Catalisi – Università degli Studi di Perugia, Italy.*
sara.stocchetti@unica.it

Natural oils and fats are essential resources in the oleochemical industry, valued for their abundance and versatile properties. They serve as sustainable raw materials for producing critical intermediates used in various industrial applications.[1] In this view, this study focuses on the oxidation of the double bond in oleic acid (OA) as a primary substrate, targeting the synthesis of azelaic acid (AA) and pelargonic acid (PA) (**Figure 1.a**). Azelaic acid is widely used in pharmaceuticals and cosmetics for its antimicrobial properties, while pelargonic acid has applications in herbicides and lubricants.[2] The process employs photooxidation catalyzed by 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4-CzIPN, **Figure 1.b**), a metal-free photocatalyst known for its efficiency in various reactions.[3] Preliminary experiments were conducted in a batch reactor, including 3D-printed setup (e.g., the "UFO")[4] and LED system (Kessil lamp), to optimize reaction efficiency and selectivity (**Figure 1.c**).

Kinetic and mechanistic studies are ongoing to identify reaction intermediates and elucidate the main pathway, with efforts focused on minimizing by-products such as aldehydes and short-chain acids. To further enhance efficiency and scalability, continuous flow technology is being integrated, enabling intensified reaction conditions. [5] This approach aims to develop a sustainable, scalable, and industrially viable process for converting natural oils and fats into valuable carboxylic acids, contributing to green chemistry and the circular economy.

Figure 1: *(a) aerobic photooxidative cleavage of oleic acid (OA); (b) structure of 4-CzIPN; (c) batch setup.*

---

[1] (a) A. E. Kerenkan *et al.*, Catal. Sci. Technol. **2016**, *6*, 971-987; (b) M. Wang et al., ACS Catal. **2018**, *8*, 2129−2165.

[2] (a) G. Cravotto *et al.*, Catalysts **2018**, *8* (10), 464; (b) L. Gardossi *et al.*, Polymers **2021**, *13*, 4091; (c) R. Ciriminna *et al.*, Biofuels, Bioprod. Bioref. **2019**, *13*, 1476–1482.

[3] T.-Y. Shang *et al.*, Chem. Commun. **2019**, *55*, 5408.

[4] T. Noël *et al.*, React. Chem. Eng. **2024**, *9*, 2218–2225.

[5] C. Sambiagio & T. Noël, Trends in Chem. **2020**, *2*, 96-106.

P53: H/D exchange of amine compounds catalyzed by cationic Iridium (III)-Cp* complexes bearing dioxime ligands using D_2O as deuterium source

Francesco Taglieri, [1] Andrea Di Giuseppe, [1] Marcello Crucianelli, [1] Lorenzo Biancalana [2]

[1] *Università dell'Aquila, Dipartimento di Scienze Fisiche e Chimiche, Via Vetoio, I-67100 L'Aquila, Italy.*
[2] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via G. Moruzzi 13, I-56124 Pisa, Italy*
E-mail: francesco.taglieri@graduate.univaq.it

The hydrogen/deuterium (H/D) exchange reaction plays a pivotal role in introducing deuterium into organic molecules, a transformation crucial for applications ranging from mechanistic studies to enhancing the ADME (Absorption, Distribution, Metabolism, and Excretion) properties of pharmaceutical compounds.[1] Amino groups, which are widely present in active pharmaceutical ingredients (APIs), are particularly susceptible to enzymatic cleavage at their α and β positions. Substituting protium with deuterium at these sites improves their stability and optimizes pharmacokinetic profiles.[2]

Despite its importance, the H/D exchange process faces significant challenges, particularly regarding the choice of deuterium sources and the development of catalytic systems. Recent advancements have focused on creating practical and cost-effective methodologies. In this context, novel Iridium(III)-Cp* catalysts featuring dioxime ligands have been synthesized and evaluated for H/D exchange reactions on amine substrates, employing D_2O as a safe, economical, and efficient deuterium source.[3]

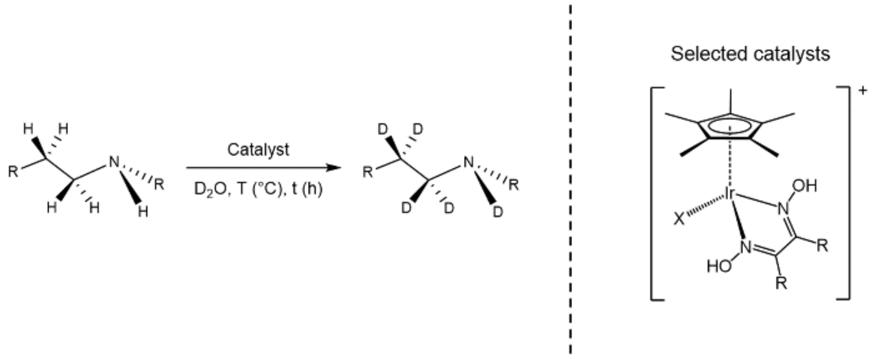


Figure 1*: General reaction scheme of Iridium catalysed H/D exchange.*

---

[1] X. L. Xu, W. Zhang, and G. W. Rao, *Curr. Med. Chem.* **2023**, *30*, 4096-4129

[2] B. Chatterjee, V. Krishnakumar, and C. Gunanathan, *Org. Lett.* **2016**, *18,* 5892-5895

[3] R. Colaiezzi, C. Saviozzi, N. Di Nicola, S. Zacchini, G. Pampaloni, M. Crucianelli, F. Marchetti, L. Biancalana, *Catal. Sci. Technol.* **2023**, *13*, 2160-2183

P54: CHEMICAL RECYCLING STRATEGIES: CATALYTIC HYDROCONVERSION OF POLYOLEFINS

Antonio C. P. Trimboli [a], Elena Groppo [b], Piero Torelli [c], Viviana Bressi [a], Emilia Paone [a], Francesco Mauriello [a]

[a] Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, IT89123 Reggio Calabria, Italy
[b] Dipartimento di Chimica, NIS Interdepartmental Research Center and INSTM Reference Center, Università degli Studi di Torino, Via G. Quarello 15A, I-10135, Torino, Italy
[c] CNR-IOM, Area Science Park Basovizza, IT34149 Trieste, Italy

antoniocp.trimboli@unirc.it

Plastics are now the most extensively produced synthetic materials in the world. By 2015, an estimated 6,300 million metric tons of plastic waste had been generated, with only 9% recycled, 12% incinerated, and an alarming 79% ending up in landfills or the natural environment. If current patterns continue, the total accumulation of plastic waste could reach 12,000 million metric tons by 2050[1]. This issue is particularly critical for common polyolefins like polyethylene (PE) and polypropylene (PP), whose mass production, low cost, and prevalent use in disposable applications have exacerbated waste management challenges. Today, only a small percentage of these materials are mechanically recycled, while most are incinerated, landfilled, or leak into the environment. Due to their high energy content, there is growing interest in recovering their chemical value and adopting more sustainable disposal methods[2].

This project seeks to address these challenges by exploring the catalytic upcycling of waste polyethylene into valuable liquid alkanes, raising both scientific and public awareness about this promising solution. Traditional thermochemical processes, such as pyrolysis and thermal cracking, break down polyolefins by cleaving the strong C−C bonds in PE, producing small molecules suitable as fuels. However, these approaches are highly energy-intensive and struggle with product selectivity. In contrast, hydroconversion, which also targets C−C bond dissociation, offers a more selective method, breaking down polyolefins into liquid alkanes within specific molecular weight ranges[3].

This study investigates polyethylene hydroconversion using two ruthenium-based catalysts: monofunctional Ru/C, which primarily supports hydrogenolysis, and bifunctional Ru/Al$_2$O$_3$, which facilitates hydrocracking. Results demonstrate that polyethylene conversion increases over time for both catalysts, with Ru/Al$_2$O$_3$ achieving notably higher conversion rates compared to Ru/C. The superior performance of Ru/Al$_2$O$_3$ is attributed to its enhanced catalytic activity, which effectively promotes hydrocracking reactions. Furthermore, Ru/Al$_2$O$_3$ consistently produces a larger fraction of hydrocarbons in the desirable C$_5$–C$_{20}$ range, making it well-suited for applications targeting this product range.

These findings highlight the efficiency of Ru/Al$_2$O$_3$ in selectively breaking down polymer chains into valuable hydrocarbons, positioning it as a more effective catalyst for polyethylene hydroconversion processes.

---

[1] R. Geyer, et al., Production, use, and fate of all plastics ever made, Sci. Adv., 3 (2017) e1700782.

[2] Jiakai Sun, Jinhu Dong, Lijun Gao, Yu-Quan Zhao, Hyunjin Moon, and Susannah L. Scott, Chemical Reviews 2024 124 (16), 9457-9579, DOI: 10.1021/acs.chemrev.3c00943.

[3] J.E. Rorrer, G.T. Beckham, Y. Román-Leshkov, Conversion of polyolefin waste to liquid alkanes with Ru-based catalysts under mild conditions, JACS. Au 1 (2020) 8–12, doi: 10.1021/jacsau.0c00041.

P55: A NOVEL CATALYST-FREE PLASMA-LIQUID ELETROCHEMICAL APPROACH FOR ACTIVATION OF SMALL MOLECULES

Lavanya Veerapuram[1], Marco Francesco Torre[1], Francesco Tavella[1], Siglinda Perathoner[1], Gabriele Centi[1], Claudio Ampelli[1] and Chiara Genovese[1]

[1] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), University of Messina, ERIC aisbl and CASPE/INSTM, Messina Italy*

lavanya.veerapuram@studenti.unime.it

Plasma-liquid systems represent an advanced and energy-efficient approach to material synthesis and chemical processing by utilizing highly reactive species generated under ambient conditions. Unlike conventional methods that typically require elevated temperatures, pressures, or catalysts to drive reactions, plasma-liquid systems provide a more effective solution for modern industrial applications. The interactions within plasma-liquid systems hold significant potential for carbon dioxide (CO_2) reduction and ammonia (NH_3) synthesis—two essential processes for addressing climate change and enhancing global chemical and fertilizer production. In this study, we present the design of a new aqueous plasma-electrochemical device with a micro-plasma jet as cathode, for application in the CO_2 reduction process and N_2 fixation, under ambient conditions. In CO_2 reduction, plasma-liquid processes generate solvated electrons that are derived from hydronium ions (H_3O^+), acting as powerful reducing agents. These electrons initiate and sustain the conversion of CO_2 into valuable products, including methanol, oxalic acid, formic acid, and syngas. These mechanisms enable effective carbon recycling by directly breaking down CO_2 molecules, thus circumventing conventional catalytic steps [1]. Similarly, in ammonia synthesis, plasma-liquid interactions produce reactive nitrogen species such as nitrogen radicals and solvated electrons that facilitate NH_3 formation at ambient conditions. This method diminishes reliance on traditional catalytic system and provides alternative pathways for nitrogen fixation, which has important implications for renewable energy [2-3].

We report here the optimization of all the operational parameters (i.e distance between plasma and liquid, gas-flow, dimension of the plasma jet etc.) to maximize the efficiency of the plasma-electrochemical device allowing to reach a FE% more than 50% for NH_3 synthesis in only after 30 minutes of reaction. For CO_2 reduction, preliminary results indicate FE more than 50% for oxalic acid after 15 minutes of reaction at ambient conditions. Although further investigation is necessary, these results are very promising as sustainable approach for small molecules activation.

Acknowledgements: *This work is funded by the EU through the SCOPE (ID: 810182) ERC Project, and by the MUR through the PRIN Project MAPEC (N. 2022599NR3), which are gratefully acknowledged.*

---

[1] A Mota-Lima, The Journal of Physical Chemistry C **2020,** 124 (20), 10907-10915

[2] P J Bruggeman, B R Locke, *et al Plasma Sources Science and Technology,* **2016,** *25*(5), 053002

[3] R Hawtof, S Ghosh, E Guarr, C Xu, R Mohan Sankaran, JN Renner *Science advances,* **2019,** 5(1):5778

P56: Hazelnut Shells waste as a sustainable source of activated carbon aimed at the manufacture of electrodes for supercapacitors

Stefania Volante,[1] Domenico Licursi,[1] Federico Maria Vivaldi,[1] Pietro Zaccagnini,[2] Federico Bella,[2] Fabio Di Francesco,[1] Anna Maria Raspolli Galletti,[1] Claudia Antonetti[1]

[1] *University of Pisa, Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, Pisa, Italy*
[2]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy*
stefania.volante@phd.unipi.it

Rising concerns over energy scarcity and fossil fuel-related pollution highlight the urgent need for advanced green energy alternatives and efficient energy storage solutions. Supercapacitors (SCs) stand out among storage devices due to their high power density, long lifespan and rapid charging. SCs are categorized into electric double-layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors (HSCs), which combine both charge storage mechanisms. [1]. EDLCs store energy by generating double-layer charges on electrode surfaces and their efficiency largely depends on surface optimization. Carbon-based materials, such as activated carbons (ACs), are commonly employed for this aim, due to their cost-effectiveness, high conductivity and large surface area [1]. In this context, biomass emerges as a promising resource for the manufacturing of electrodes, by yielding carbonaceous chars through thermal processing. Conversely, pseudocapacitors store energy through rapid reversible redox reactions, utilizing various metal oxides [1]. Notably, CuO is particularly appealing, due to its high theoretical pseudocapacitance and good conductivity. Therefore, the development of composite materials made with carbon chars including CuO may represent a promising solution for the fabrication of new electrode materials with high performance and stability [2]. In this work, hazelnut shell (HS) biomass has been employed as the precursor for the synthesis of new ACs. Specifically, a three-step procedure was proposed, including 1) a hydrothermal carbonization step (220 °C for 5 h), followed by 2) pyrolysis (600 °C for 1h) and 3) KOH activation (600 °C for 1 h) [3]. In addition, other new ACs have been synthesized, *i)* the AC from the direct activation of the raw HS (HS-AC) and *ii)* that originating from the activation of the hydrochar (HTC-AC). After evaluating their electrochemical properties through cyclic voltammetry and galvanostatic charge-discharge measurements, a post-modification procedure was proposed for the best-performing ACs, utilizing CuO to enhance their final performances. This work highlights the real possibility of using the obtained chars for the production of SC electrodes, promoting an eco-friendly waste biomass valorization, aimed at improving the circular economy.

Acknowledgements: The authors are grateful to the European Union and Italian "Ministero dell'Istruzione, dell'Università e della Ricerca" for the financial support provided through the PNRR project Sustainable Mobility Center CNMS, Spoke 13 Electric Traction Systems and Batteries (ETSB), CUP I53C22000720001.

---

[1] Poonam, K. Sharma, A. Arora, S.K. Tripathi, *J. Energy Storage*, 21, 801-825, **2019**.
[2] Y. Zhan, J. Bai, F. Guo, H. Zhou, R. Shu, Y. Yu, L. Qian, *J. Alloys Compd*, 885, 161014, **2021**.
[3] D. Licursi, C. Antonetti, N. Di Fidio, S. Fulignati, P. Benito, M. Puccini, S. Vitolo, A.M. Raspolli Galletti, *Waste Manag.*, 168, 235-245, **2023**.

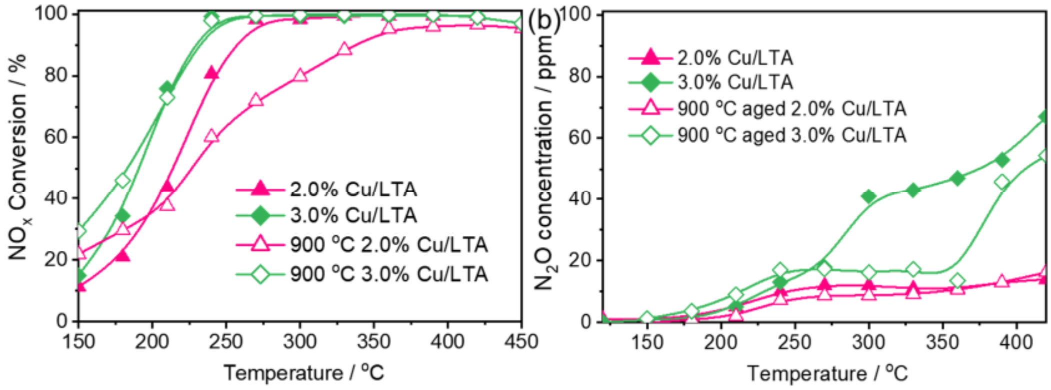
P57: Investigating High Thermal Stability and CO Adsorption Behavior in Cu/LTA Zeolites for NO_x Abatement Applications

<u>H. Yu,</u>[1,2] C. Nannuzzi,[2] E. Borfecchia,[2] R. Abasabadi,[2] J. Zhang,[1] D. Peng,[1] D. Zhang,[1*] S. Bordiga,[2*] G. Berlier[2*]

[1]Department of Chemistry, College of Sciences, Shanghai University, 200444 Shanghai, China
[2] Dipartimento di Chimica & NIS Centre, Via P. Giuria 7, I-10125 Torino, Italy
dszhang@shu.edu.cn, silvia.bordiga@unito.it, gloria.berlier@unito.it

Copper-exchanged zeolites (Cu-zeolites) have gained attention for their excellent performance in selective catalytic reduction (SCR) reactions for NO_x removal.[1] Although CHA-type zeolites (Cu-CHA) are widely used in emission control systems for automotive and industrial applications, their stability under prolonged high-temperature conditions, particularly in the presence of water, remains a significant challenge, often resulting in the deactivation of active sites and potential structural degradation.[2] To overcome these challenges, high Si/Al ratio LTA-type zeolites (Cu/LTA) have emerged as promising alternatives, exhibiting improved hydrothermal stability and structural integrity even after aging at temperatures up to 900°C.[3] This study investigates the CO adsorption behavior and thermal stability of high Si/Al ratio Cu/LTA zeolites, focusing on the role of Cu(I) and Cu(II) redox cycles, which are essential for efficient SCR performance. Through CO adsorption experiments and additional characterization techniques, including infrared spectroscopy (IR) and nitrogen physisorption (BET), we examine the distribution and stability of Cu(I) active sites in aged Cu/LTA. These findings provide valuable insights for optimizing Cu/LTA as a durable SCR catalyst, supporting the development of more effective NOx reduction technologies for emission control systems.

Figure 1*. Plots of NOx conversion(a) and N_2O concentration(b) versus temperature over Cu/LTA catalysts.*



Test conditions: $NO_x = NH_3 = 500$ ppm, $[O_2] = 10$ vol%, $[H_2O] = 5$ vol%, $[CO_2] = 5$ vol%, N_2 as balance, WHSV = 100, 000 $mL \cdot g^{-1} \cdot h^{-1}$.

---

[1] A. Wang et al., *Appl. Catal. B* **2019,** *246* 242–253.
[2] T. Ryu, et al., *Appl. Catal. B* **2019,** *245* 513–521.
[3] T. Ryu, et al., *Angew. Chem. Int. Ed.* **2017,** *56* 3256–3260.

Organizing Institutions

Società
Chimica
Italiana
Gruppo Interdivisionale di Catalisi

EFCATS
European Federation
of Catalysis Societies

UNIVERSITÀ
DEGLI STUDI
DELL'AQUILA

INSTM

Organizing Committee

Chair

Marcello CRUCIANELLI
University of L'Aquila

Co-Chair

Armando CARLONE
University of L'Aquila

Alfredo ALOISE
University of L'Aquila

Alessandra BIANCOLILLO
University of L'Aquila

Maria Edith CASACCHIA
University of L'Aquila

Andrea DI GIUSEPPE
University of L'Aquila

Nicola DI NICOLA
University of L'Aquila

Elena GROPPO
University of Turin

Debora IAPADRE
University of L'Aquila

Andrea LAZZARINI
University of L'Aquila

Francesco MAURIELLO
University of Reggio Calabria

Fabio PESCIAIOLI
University of L'Aquila

Sara SCIARRETTA
University of L'Aquila

Scientific Committee

LOCAL SCIENTIFIC COMMITTEE

Armando CARLONE (UnivAQ)
Marcello CRUCIANELLI (UnivAQ)
Andrea DI GIUSEPPE (UnivAQ)
Andrea LAZZARINI (UnivAQ)
Fabio PESCIAIOLI (UnivAQ)

NATIONAL SCIENTIFIC COMMITTEE

Alessandro TROVARELLI (UniUD)
Elena GROPPO (UniTO)
Francesco MAURIELLO (UniRC)
Federica MENEGAZZO (UniVE)
Tommaso TABANELLI (UniBO)
Silvia BORDIGA (UniTO)
Matteo GUIDOTTI (CNR-SCITEC)
Rinaldo PSARO (CNR-SCITEC)
Marcello CRUCIANELLI (UnivAQ)

Diamond Sponsor

Platinum Sponsor

Dompé

Gold Sponsor

Cabro
TRADITION & INNOVATION

VERDER

Silver Sponsor

REGIONE
ABRUZZO

GENTIUM VEL FORTISSIMARUM ITALIAE

CONSIGLIO REGIONALE

Since 1949
Dipharma

indena®
100+
YEARS

SCIENCE IS OUR NATURE. SINCE 1921

Supporters

ROYAL SOCIETY
OF **CHEMISTRY**

Chemistry
A European
Journal

Chemistry
Europe

FONDAZIONE
CASSA DI RISPARMIO
DELLA PROVINCIA DELL'AQUILA